LOW TEMPERATURE CONDENSATION OF HIGH TEMPERATURE SPECIES AS A SYNTHETIC METHOD

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I. Introduction

The idea of studying gaseous radicals and high temperature species by condensing them on very cold surfaces, has been employed for many years. The work of Rice and Freamo (*77*) on the thermal decomposition of hydrazoic acid was a spectacular example. The imine radical produced condensed to a bright blue solid at −196° which on warming to room temperature formed white ammonium azide. Various methods of trapping unstable species were reviewed in 1960 in a book by Bass and Broida (*5*).

An important development occurred in 1963 when Skell and Westcott (*106*) reported that carbon vapor, formed from a carbon arc under vacuum, reacted with organic compounds at −196° to give new compounds incorporating the carbon vapor species. The objectives of these experiments and the reaction conditions used are fundamental to the work discussed in this chapter.

The carbon was vaporized under high vacuum so that the vapor species could move away from the arc without intermolecular collisions which would have caused aggregation. The walls of the surrounding vacuum chamber were cooled with liquid nitrogen. This allowed the vapor of another compound to be passed into the chamber while the carbon was evaporating and to be condensed on the walls so rapidly that high vacuum conditions were maintained. Even with substantial rates of addition of the compound, very little of it contacted the hot carbon or interacted with carbon vapor species until the moment of condensation on the walls. The carbon vapor reacted with the other compound on the cold walls provided that thermodynamic and kinetic factors were favorable. The experiments were conducted on a scale which enabled any new compounds formed to be isolated and characterized.

This work marked the beginning of a new and fruitful phase in the exploitation of low temperature condensation reactions of high temperature species as a useful synthetic method. Since then, at least twenty atomic and molecular high temperature species have been used as reagents in chemical synthesis under conditions closely related to those described by Skell and Westcott, and many new compounds have been synthesized.

The major portion of this chapter is a review of the formation and reaction of those species which have been used in synthesis, but the total range of available species and the special features of low temperature condensation reactions are discussed first.

Most of the species considered will have been made at temperatures above 1000°, at pressures below 1 Torr, and in approximate thermal equilibrium with their surroundings. The last is a particularly important limitation in scope. Reactive chemical species can be formed by a variety of nonthermal methods including electrical discharges, photochemical excitation, and nuclear recoil. Such methods cause excitation of atoms and molecules and the formation of "high temperature" species. Usually these species are in no sense in thermal equilibrium with their surroundings (Section VI). However, the definition of approximate thermal equilibrium is broad and includes, for example, electronically excited carbon vapor species formed from an arc.

II. Species and Reaction Conditions

There are many gaseous atomic and molecular species which are thermodynamically stable with respect to condensed phases or other gaseous molecules only at high temperatures. These species have mostly been first characterized spectroscopically, and frequently equilibrium data for their formation have been obtained by mass spectrometric, effusion, and transpiration studies (*55*).

To be of interest to a synthetic chemist hoping to apply the low temperature condensation procedure, a high temperature species should meet two requirements. First, it must contain an element in a form which for thermodynamic and kinetic reasons is liable to be reactive at low temperatures. Second, it must be possible to form the species in a fairly pure state at the rate of at least a few millimoles an hour.

A. ATOMIC SPECIES

The largest single class of species which clearly meet the above criteria is the atoms of the elements. A gaseous atom of any element except the noble gases may be expected to be more reactive than the normal form of the element for two reasons. First, the atom can react faster because it has minimal steric requirements and generally has readily available electrons or orbitals. Second, the atom is a species of higher energy than the normal state of the element. This is shown in Table I which gives the heats of formation of the gaseous atoms of the elements relative to their standard states at 25°. Condensation of the atoms in an isolated

TABLE I

HEATS OF FORMATION ($\Delta H_{298°K}$) OF GASEOUS ATOMS OF THE ELEMENTS[a]

H	Li	Be											B	C	N	O	F	Ne
52	39	78											134	171	113	59	19	0
	Na	Mg											Al	Si	P	S	Cl	Ar
	26	35											78	107	79	67	29	0
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	21	42	82	113	123	95	67	100	101	103	80	31	69	90	72	54	27	0
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	20	39	86	145	172	159	(155)	155	133	89	68	27	58	72	63	47	25	0
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	19	42	104	145	187	202	186	187	160	135	88	15	43	47	50	34	—	0

[a] Values in kcal/mole. Data from reference (*67a*), and compilation by Honig (*33a*).

form on an inert surface at −196° will not greatly change their energy, so that the values in Table I can be used when considering the energetics of low temperature condensation reactions. The extra energy possessed by atoms compared with the normal states of the elements will always make some difference to their chemistry, but a large difference is not likely until the atoms have heats of formation greater than about 40 kcal/mole. Then the atoms can react via intermediates far too endothermic to be formed from the normal states of the elements under reasonable conditions.

Thus, a reaction reported by Skell and Engel (*92*) in which butenes, butadiene, and methylcyclopropane were formed from carbon atoms and propane, would be impossible for solid carbon on both thermodynamic and kinetic grounds. On the other hand, none of the reactions reviewed by Mile (*65*) involving alkali metal atoms, which have quite low heats of formation, would have been thermodynamically impossible starting with the solid metals, only kinetically less favored.

The change in potential reactivity of elements on atomization can be further illustrated by considering the reaction of copper or sodium atoms with chlorine-containing compounds. The heats of formation of solid sodium chloride and cuprous chloride are about −98 and −32 kcal/mole, respectively, so that reactions of sodium with chlorine-containing compounds are normally much more exothermic than reactions of copper. However, the Na–Cl and Cu–Cl bond dissociation energies are much closer in value, about 98 and 87 kcal/mole, respectively. The difference between these two sets of values is almost all accounted for by the higher heat of formation of gaseous copper atoms. The implication is that when copper atoms are condensed with chlorine-containing compounds on a cold surface, they may be nearly as effective dechlorinating agents as sodium atoms (Section V,D).

Atoms of some elements, particularly those which vaporize at low temperatures in molecular forms, are not as conveniently made by thermal dissociation as by other excitation methods such as an electrical discharge (Section VI,A). The lifetimes in the gas phase of atoms of these elements are generally much longer than, for example, gaseous metal atoms. It is possible to pump atomic nitrogen at a pressure of a few Torr along tubing in a vacuum system with only slow recombination (*140*), whereas nickel atoms will condense immediately on collision with a surface at room temperature.

Electronically excited states of atoms will be energetically even further above the normal state of elements than are the ground state atoms. The population of excited states among atoms formed by purely thermal means below 3000° is usually low, but it may be considerable in atoms formed by electrical discharge or photochemical methods. Skell and his associates (*91*, *93*, *107*), in their work with carbon vapor formed in an arc, have shown that different electronic states of carbon vapor species have different chemical reactivities at −196°. The lifetimes of the excited states are long enough to survive the time interval between generation in the arc and arrival on a cold surface (Section IV,B). Some excited states of transition metal atoms may be very short-lived ($<10^{-9}$ sec) and could undergo radiative decay before reaching a cold surface.

B. MOLECULAR SPECIES

1. *Formation*

As there is a wide variety of known high temperature molecular species, the selection of those of possible synthetic use is more difficult than with atomic species.

Molecular species which can be formed at high temperatures in useful amounts for synthesis generally fulfill two conditions. First, the species contain strong bonds which prevent them from undergoing dissociation to the elements at the temperature at which they are formed. Second, the process by which they are formed involves an increase in the number of gas molecules so it is favored by increasing the temperature and lowering the pressure. These conditions rule out many species known to spectroscopists which can be formed only in tiny concentrations, e.g., transition metal hydride vapors (*19*).

Some different processes which allow high temperature species to be formed with an increase in the number of gas molecules are shown below:

(*a*) The evaporation of solids or liquids, e.g.,

$$\mathrm{CaF_2(s)} \xrightarrow[10^{-2}\ \mathrm{Torr}]{1300^\circ} \mathrm{CaF_2(g)} \qquad \text{ref. } (\mathit{18}) \tag{1}$$

$$\mathrm{C(s)} \xrightarrow[10^{-2}\ \mathrm{Torr}]{2500^\circ} \mathrm{C_1(g) + C_2(g) + C_3(g)} \qquad \text{ref. } (\mathit{86}) \tag{2}$$

(*b*) Solid-solid or solid-liquid reactions, e.g.,

$$\mathrm{Si(s) + SiO_2(s)} \xrightarrow[10^{-2}\ \mathrm{Torr}]{1350^\circ} \mathrm{2SiO(g)} \qquad \text{ref. } (\mathit{13}) \tag{3}$$

$$\mathrm{2B(s) + 2B_2O_3(l)} \xrightarrow[10^{-2}\ \mathrm{Torr}]{1300^\circ} \mathrm{3(O{=}B{-}B{=}O)\ (g)} \qquad \text{ref. } (\mathit{40}) \tag{4}$$

(*c*) Gas-solid reactions, e.g.,

$$\mathrm{2B(s) + BF_3(g)} \xrightarrow[1\ \mathrm{Torr}]{2000^\circ} \mathrm{3BF(g)} \qquad \text{ref. } (\mathit{31}) \tag{5}$$

$$\mathrm{2B(s) + 2H_2S(g)} \xrightarrow[1\ \mathrm{Torr}]{1200^\circ} \mathrm{2HBS(g) + H_2} \qquad \text{ref. } (\mathit{44}) \tag{6}$$

(*d*) Dissociation of gases, e.g.,

$$P_2F_4(g) \xrightarrow[10^{-3}\text{Torr}]{900^\circ} 2PF_2(g) \quad \text{ref. } (111) \qquad (7)$$

$$S_8(g) \xrightarrow[10^{-3}\text{ Torr}]{1000^\circ} 4S_2(g) \quad \text{ref. } (86) \qquad (8)$$

Some condensed phases vaporize both as monomeric and polymeric species, the proportion of polymers in the saturated vapor increasing with increasing temperature (*51*). This only occurs when the heat of dimerization is less than the heat of vaporization of the element or compound in a monomeric form. An element like carbon with a very high heat of vaporization as a monomer but with strong bonds in its gaseous polymers will have a considerable concentration of polymers in its saturated vapor at high temperatures.

2. *Species in Unstable Low Valencies*

Equations (2), (3), (5), and (7) show the formation of low valency species unstable with respect to a higher valency of an element at ordinary temperatures. The potential in chemical synthesis for these compounds is derived from their possible conversion to the higher valency state by reaction with other compounds. Thus, a compound like boron monofluoride readily combines with a variety of organic and inorganic compounds on being condensed with them at −196°, to form

TABLE II

SOME GASEOUS HIGH TEMPERATURE SPECIES OF POSSIBLE INTEREST IN CHEMICAL SYNTHESIS AT LOW TEMPERATURES

Atoms[a]	*Halides*	*Oxides, sulfides, nitrides, carbides*
Atoms of all elements except the noble gases (see Table I)	Nonmetals	Nonmetals
Homonuclear molecules	BF,[a] BCl[a]	B_2O_2,[b] B_2O_3[b]
C_2,[a] C_3,[a] C_4[a]	CF_2,[a] CCl_2,[a] CBr_2[a]	HBS,[b] BC_2[a]
P_2,[b] As_2,[b] Sb_2[b]	SiF_2,[a] $SiCl_2$,[a] $SiBr_2$[a]	CS[a]
S_2,[b] Se_2[b]	PF,[a] PF_2[a]	SiO,[a] SiS,[a] SiC[a]
	Metals	GeO,[b] GeS[b]
	LiF,[b] CaF_2,[b] AlF_3[b]	PN[b]
	AlF,[a] ScF,[a] $LaCl$[a]	Metals
	TiF_2,[b] ZrF_2,[b] CrF_2[b]	BeO,[b] TiO[b]
		ZrO_2[b]

[a] Species containing elements in unstable low valency states.

[b] Species containing elements in valency states in which they are commonly stable at ordinary temperatures.

a derivative of trivalent boron (*119*) (Section IV, A). Reactions of boron monofluoride with other compounds are able to compete successfully with its tendency to react with itself to give $(BF)_n$ or to disproportionate to boron and boron trifluoride. The heat of formation of boron monofluoride from boron and boron trifluoride is roughly 60 kcal/mole (*10*), and this can be taken as a crude measure of its instability relative to trivalent boron at low temperatures.

Unfortunately, not all low valency species are as reactive as boron monofluoride. For some, polymerization of disproportionation occur in preference to reactions with other compounds. There is as yet insufficient data to predict the synthetic usefulness of species, although the problem is considered again in Sections IV and V.

Table II includes a selection of known low valency gaseous high temperature species which can be formed in an least millimole quantities at temperatures above 1000°, and which appear to have potential in chemical synthesis. The inclusion of a species in Table II does not mean that equilibrium high temperature methods are the only ways of making it. An example is carbon difluoride, which can be made from trifluoromethane at 1300° (*132*), but is much more conveniently made by decomposition of difluorodiazirine, CF_2N_2, at 150° (*67*) and from numerous other compounds at temperatures below 200° (*124*).

3. *Species in Normal Valencies*

Equations (1), (4), (6), and (8) show the formation of high temperature gaseous species in which the elements concerned are in valence states commonly stable at ordinary temperatures. Condensation and polymerization of these species does not involve a change in valency. The species are representatives of a large class including many metal halides, oxides, sulfides, and some homonuclear species as shown in Table II.

The potential of these species to be reagents in low temperature condensation reactions is less clear than for low valency or atomic species. It depends on whether or not effective use can be made of the energy difference between the gaseous species and the condensed, polymerized forms. For example, the heat of vaporization of zirconia is about 175 kcal/mole so that $ZrO_2(g)$ is very unstable with respect to $ZrO_2(s)$ at ordinary temperatures. It is possible that on low temperature condensation $ZrO_2(g)$ may react with acids, alcohols, etc., to which solid zirconia is very resistant. On the other hand, polymerization of $ZrO_2(g)$ to $ZrO_2(s)$ may be the only observed process under all condensation conditions. Although there is no experimental evidence yet with $ZrO_2(g)$, there are indications that at least some of the high temperature species in this class are reactive (Section IV).

4. *The Lifetimes of Species in the Gas Phase*

Species formed by vaporization of condensed phases at high temperatures will generally condense immediately on contact with solid surfaces at ordinary temperatures. This includes species formed by reactions in condensed phases such as SiO, B_2O_2, and AlF.

A greater variation in lifetime comes with molecular species formed by reactions involving gases at high temperatures. For example, silicon dichloride formed from silicon and silicon tetrachloride is a short-lived species in the gas phase. At a pressure of 0.1 Torr it will decay in a few milliseconds forming $(SiCl_2)_n$ on contact with solid surfaces, or reacting rapidly with any silicon tetrachloride present to form perchlorosilanes (*122*). Silicon dibromide is similarly short-lived. In contrast, silicon difluoride has a half-life of about 150 sec at 0.1 Torr pressure (*130*) and it decays only on solid surfaces forming $(SiF_2)_n$, not perfluorosilanes. This striking difference in behavior between SiF_2 and $SiCl_2$ may be caused by very slight differences in electron density on the silicon atoms in the two molecules.

Other long-lived species are HBS (*44*) and PF_2 (*111*). The long lifetime of the former is particularly surprising in view of the short lifetime of HBO (*74*).

C. OTHER FACTORS INFLUENCING LOW TEMPERATURE CONDENSATION REACTIONS

1. *Temperature and Activation Enthalpy*

As has already been illustrated, the use of low temperatures for reacting high temperature species with other compounds is dictated by practical considerations. Under no other set of conditions can the high temperature species be brought into contact with an ordinary compound on a large scale without thermal cracking of the compound or prior aggregation of the species. It is easiest to maintain the required high vacuum conditions if the temperature used for condensation is such that the vapor pressure of all the condensed species is less than about 10^{-5} Torr. For the majority of inorganic and organic compounds which are reacted with high temperature species, this condition is fulfilled within the temperature range $-78°$ (solid CO_2) to $-196°$ (liquid N_2). Much lower temperatures, which can be obtained using liquid hydrogen (20°K) or liquid helium (4°K), are only practical for very small-scale work.

Reaction rates are strongly affected by the activation enthalpy at low temperatures. For example, at $-196°$, assuming an activation entropy of $-10\ \text{cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$, the rate constants for reactions of activation enthalpies 1, 2, and 5 kcal/mole are very roughly 10^7, 10^4, and 10^{-4} sec^{-1}, respectively. High temperature species are observed to polymerize very rapidly on cold surfaces which indicates that these reactions may have activation enthalpies of 1 kcal/mole or less. Thus, activation enthalpies of reactions between high temperature species and ordinary compounds have to be similarly low if the reactions are to compete with polymerization of the high temperature species. Raising the temperature of the cold surface reduces the differences in reaction rates caused by small differences in activation enthalpy. The corresponding rate constants for the above reactions at −78° are very roughly 10^9, 10^8, and 10^5 sec^{-1}, respectively. This suggests that the temperature chosen for the condensation should be as high as possible. This was demonstrated by results of Bassler *et al.* (*6*). However, the best temperature will be a compromise between these kinetic effects and the practical considerations of available coolants, the need for low vapor pressures, and the preservation of unstable reaction products.

2. *The Process of Condensation*

There are three main ways in which a short-lived high temperature species can be brought into contact with another compound on a cold surface.

(*a*) The species and a compound with which it may react are cocondensed, i.e., condensed simultaneously, on the cold surface. This is the method which has already been described and which has been used most commonly in synthetic work.

(*b*) The species and at least a hundredfold excess on an inert gas are cocondensed on the cold surface, to isolate the species in an inert matrix. A compound which may react with the species is then condensed on the matrix and is allowed to diffuse into the matrix on warming.

(*c*) The species is condensed on to a cold sample of a potentially reactive compound in a solid, liquid, or solution form.

When a high temperature species and another vapor are cocondensed on a cold surface, several processes occur. At the moment of impact on the surface all the molecules immediately lose most of their translational energy and will very rapidly lose their excess rotational and vibrational energy. However, the surface will be in a fluid state and the molecules will move around for a short time. The period of surface motion is shorter the lower the temperature of the cold surface.

In most cases it is not known what proportion of the molecules of the high temperature species react in this stage of surface mobility, but evidence from matrix isolation experiments (see below) suggests almost complete reaction. The primary products of the reactions and unchanged reactants will then be frozen on the surface and covered by other molecules. Secondary reactions may occur when the temperature is raised at the end of the cocondensation to give the products which are finally isolated at ordinary temperatures. In several of the reactions discussed in Sections IV and V, it is noted that some obvious change, such as evolution of gas, occurred on warming to slightly above −196°.

The yields in cocondensation reactions can nearly always be improved by using a large excess of the compound condensed with the high temperature species as this reduces the proportion of contacts between molecules of the high temperature species.

Method (*b*) depends on being able to prevent polymerization of a high temperature species by surrounding it with many inert atoms or molecules in a rigid matrix. Because of the surface mobility problem discussed above, this is not easily achieved. Skell and his associates (*90*, *91*, *93*, *107*) were successful in isolating small quantities of carbon vapor species in neopentane matrices at −196° and subsequently reacting these with other compounds. However, Brewer *et al.* (*12*) failed to isolate metal atoms in sulfur hexafluoride on cocondensation at −196°. They found that by condensing the atoms and SF_6 at −250°, using a very large excess of SF_6, they obtained isolated atoms which remained isolated on warming to −196°.

Matrix isolation of high temperature species in noble gas matrices at 4° or 20°K is a technique which has been used widely by spectroscopists (*63*, *136*). It is possible to condense and isolate another compound along with the high temperature species in an inert matrix, and watch changes in the spectrum when diffusion is allowed to occur at a higher temperature. However, this powerful method has so far been applied to only a few of the reactions of interest to synthetic chemists (*6*).

Method (*c*) works well if a high temperature species is condensed into a cold, stirred liquid or solution (*89*). This is a very attractive alternative to method (*a*) for synthetic work when liquids of suitable vapor pressure can be chosen. Reaction of the high temperature species probably occurs in the surface layers of the liquid just as it occurs on a surface used for cocondensation. When a high temperature species is condensed on a cold solid, reaction seldom occurs. The species simply polymerizes on the surface. Hydrogen atoms are known to diffuse into solid olefins at −196° (*46*), but these are exceptionally mobile.

III. Experimental Methods

The basic experimental requirements for studying low temperature reactions of high temperature species are a furnace for generating the species inside a vacuum system and a cold surface on which the species can be condensed with other compounds.

The design of an apparatus will be influenced by many variables such as the method of formation of the high temperature species, the lifetime of the species in the gas phase, the manner in which the species is condensed with other compounds, and the scale on which the experiment is to be run.

A. THE FORMATION OF HIGH TEMPERATURE SPECIES

1. *Preparation from Condensed Phases*

A considerable technology exists on the vacuum evaporation of metals, metalloids, and other condensed phases, developed by chemists and physicists interested in thin films of these materials (*32*). Experimentally the methods fall into two groups depending on whether or not the substance being vaporized is in contact with other hot materials. In almost all cases, the high temperature species formed are short-lived and must travel to a cold surface by a line-of-sight path.

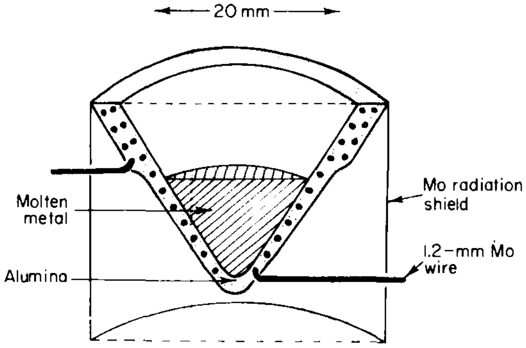


FIG. 1. Section through crucible used for evaporating metals.

a. Methods Employing a Hot Container. The range of materials which can be used as containers at high temperatures is rather limited. The requirements are a high melting point and resistance to corrosion. The latter is a formidable problem when heating many elements and compounds—hence the need for the "containerless" methods discussed below.

A type of container which the author has found particularly useful is shown in Fig. 1. This is a crucible made from a spiral of molybdenum wire coated with alumina cement. It is heated by passing an electric current through the wire. The design is a development of that described by Olsen *et al.* (*70*). The size of crucible shown in Fig. 1 conveniently holds about 0.3 ml of molten metal. The metal is heated until its vapor pressure is 10^{-2} Torr or greater before rapid evaporation occurs. For example, 2 gm of cobalt were vaporized from the crucible under high vacuum in 30 min at a temperature of about 1650° with a power input

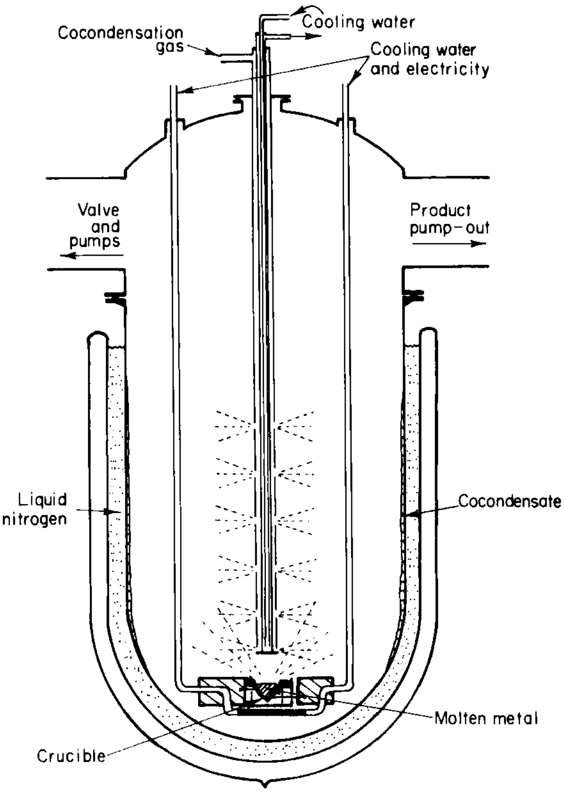


FIG. 2. Apparatus for condensing metal atoms with volatile compounds.

of 190 W. With the crucible mounted as shown in Fig. 2, roughly 90 W were radiated to the walls of the surrounding vacuum chamber, the rest of the heat was absorbed in water cooling. A larger version of the crucible with straight sides has been used to evaporate 30 gm of copper in 1 hr with a power input of 320 W.

The crucibles have been used successfully to evaporate Mn, Fe, Co, Ni, Cu, Ag, Au, and Sn as shown in Table III. Chromium has been

TABLE III

Formation of High Temperature Species Which Have Been Used in Synthesis

Species	Formed from	Temperature	Method of heating	Rate of formation (mmoles/hr)	Refs.
1. *Vapors of Main Group Elements*					
B	B(l)	2300°–2500°	Electron bombardment	~50	(*120*)
$C, C_2, C_3, \ldots$	C(s)	2600°–3200°	10–16 V ac arc	30–120	(*22*, *107*, *133*)
		~2600°	Resistance heated C rod	<20	(*112*)
Si	Si(l)	1500°–1700°	Electron bombardment	~50	(*45*)
	Si(s)	1350°	Resistance heated Si rod		(*99*)
Ge	Ge(l)	~1400°	Resistance heated graphite cloth strip	~20	(*64*)
Sn	Sn(l)	1400°	Resistance heated Mo-wound Al_2O_3 crucible	20–100	(*64*)
Mg	Mg(s)	700°	ac arc	—	(*88*)
H	H_2 (0.03–1.0 Torr)	1800°	Resistance heated tungsten strip		(*46*)
2. *Vapors of Transition Metals*					
Cr	Cr(s)	1450°	Resistance heated Mo-wound Al_2O_3 crucible	20	(*126*, *127*)
Mn	Mn(l)	1100°	Resistance heated Mo-wound Al_2O_3 crucible	20–100	(*126*, *127*)
Fe	Fe(l)	1550°	Resistance heated Mo-wound Al_2O_3 crucible	20–40	(*126*, *127*)
Co	Co(l)	1600°	Resistance heated Mo-wound Al_2O_3 crucible	20–60	(*126*, *127*)

(*continued*)

TABLE III—*continued*

Species	Formed from	Temperature	Method of heating	Rate of formation (mmoles/hr)	Refs.
Ni	Ni(l)	1600°	Resistance heated Mo-wound Al_2O_3 crucible	20–40	(*126*, *127*)
Pd	Pd(l)	1600°	Resistance heated Mo-wound Al_2O_3 crucible	10–20	(*127*)
Cu	Cu(l)	1400°	Resistance heated Mo-wound Al_2O_3 crucible	20–400	(*127*, *128*)
			Resistance heated Mo strip	10–20	(*121*)
Ag	Ag(l)	1200°	Resistance heated Mo strip	10–20	(*121*)
Au	Au(l)	1300°	Resistance heated Mo-wound Al_2O_3 crucible	10	(*28*)
3. *Gaseous Compounds*					
BF	B(s) + BF_3 (1 Torr)	1800°–2000°	Induction heated graphite tube	100	(*119*)
B_2O_2	B(s) + B_2O_3(l)	1300°–1400°	Resistance heated Mo-wound Al_2O_3 crucible	50	(*128*)
CCl_2	$HCCl_3 \rightarrow HCl + CCl_2$	1400°	Resistance heated graphite tube		(*89*)
SiF_2	Si(s) + SiF_4 (1 Torr)	1200°	Kanthal-wound quartz or mullite tube	30–300	(*130*, *131*)
$SiCl_2$	Si(s) + $SiCl_4$ (1 Torr)	1350°	Induction heated graphite tube	30	(*122*)
SiO	Commercial solid "SiO"	1400°–1500°	Resistance heated Mo-wound Al_2O_3	100–250	(*80*)
PF_2	$P_2F_4 \rightarrow 2PF_2$	800°–1000°	Resistance heated nichrome wound quartz tube	20	(*109*, *111*)

evaporated, but with slight contamination from lower aluminum oxides. More electropositive elements than chromium attack the alumina rapidly and cannot be evaporated this way. The highest temperature to which the crucible can be used is 1800°. As a consequence, it is found that metals with heats of vaporization greater than about 110 kcal (Table I) cannot be evaporated at a useful rate.

Induction heating of crucibles has been used to a limited extent. Weltner (*136*) has described a very simple induction furnace for depositing high temperature species in matrices of inert gases. Electron bombardment heating of crucibles and Knudsen cells has been used extensively in high temperature mass spectrometry (*55*) where the attainment of a very uniform, controllable temperature is important.

b. Containerless Methods. The essential feature of "containerless" methods is the introduction of energy in such a way that the material being evaporated is in contact only with cooler portions of itself or with a water-cooled metal surface with which it will not react. Such methods are mandatory for the evaporation of boron, carbon, and other elements which react with almost all possible container materials at the temperatures at which they vaporize. Containerless methods are also important for vaporizing the more refractory second- and third-row transition metals.

The most widely used containerless method for high vacuum evaporation is electron bombardment heating using a focused electron beam. An intense beam of electrons striking any solid surface will cause local heating and then vaporization. The author has used an electron gun made by Varian Associates. This draws electrons from a hot tungsten filament with a 4000-V potential and bends the electron stream through 180° magnetically to bring it to focus on a 3-mm diameter spot. The maximum power available is 2 kW. The material being vaporized is in contact only with the water-cooled body of the gun. The fastest rates of evaporation are obtained with materials which are poor conductors of heat. Using the arrangement shown in Fig. 3 in which a rod of material is fed downward into the electron beam, boron and silicon have each been vaporized at rates of about 50 mmoles/hr (*45*, *120*). These were maximum rates compatible with retention of a drop of molten material on the end of the rod. Although the main effect of the electrons is to raise the temperature of the material they strike, there is some risk of electronic excitation or even ionization of the resulting vapor.

Heating methods such as a laser beam or focused energy from the sun or from an arc are not easily used for continuous vaporization under vacuum, as vaporized material tends to coat the window through which energy passes into the vacuum system. Schaeffer and Pearson (*78*) have used a pulsed laser to vaporize small amounts of carbon and boron in the presence of other compounds.

Carbon is one of the few elements which can be evaporated successfully from an arc under high vacuum. The type of apparatus used by Skell and his associates, and other workers (*8*, *21*, *22*, *107*), is shown in Fig. 4. Using a potential of 10–16 V and a current of 30–100 A, the carbon was vaporized at a rate of 40 to 150 mmoles/hr. The carbon vapor species were formed in ground and excited electronic states (*91*, *107*), which would not be produced in a purely thermal process.

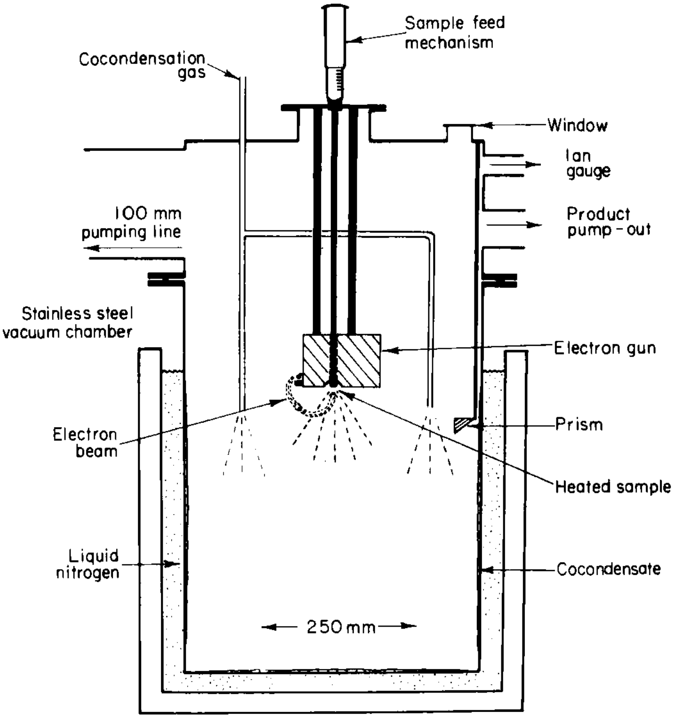


FIG. 3. Electron bombardment vaporization apparatus.

There have also been reports of evaporation of carbon (*112*) and silicon (*99*) by electrical resistance heating of a filament or rod of these materials. This is difficult to control, particularly for silicon, which melts only slightly above the temperature at which appreciable vaporization occurs.

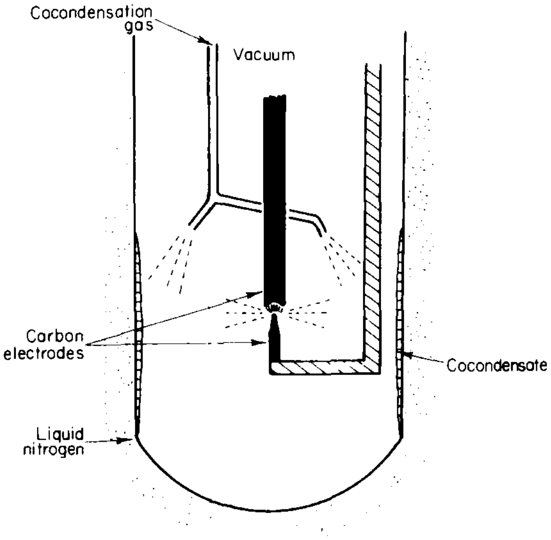


FIG. 4. Schematic of carbon arc apparatus.

2. *Preparation from Gases*

The formation of high temperature species by thermal dissociation of gases or by gas–solid reactions is most commonly carried out in a heated tube. The tube must be chemically resistant to the gas and to any condensed phase present. Unlike gaseous species formed by evaporation from condensed phases, some species formed from gases will survive collisions with cool surfaces or other gas molecules, without immediate condensation or polymerization (Section II). Thus, very high vacuum conditions and line-of-sight paths to cold surfaces are not always essential.

Figure 5 shows an apparatus which has been used for forming the relatively long-lived species, silicon difluoride (*123*, *130*). The silicon was heated inside an evacuated quartz tube by an external tube furnace. Silicon tetrafluoride was passed up through the column of hot silicon and the off-gases containing SiF_2 and SiF_4 were pumped into a liquid nitrogen-cooled trap where they could be condensed with other compounds. The pressure above the silicon was maintained at 0.1–0.2 Torr.

A similar furnace system with an alumina tube was used by Kirk and Timms (*44*) to prepare thioborane, HBS, from boron and H_2S.

Figure 6 shows an apparatus used for preparing short-lived species such as $SiCl_2$ or BF by gas–solid reactions. A graphite tube containing silicon or boron was heated inductively from a 450-kHz supply with a work coil mounted inside the vacuum system. Other designs (*119*, *125*) have put the work coil outside the vacuum chamber. The vapors of the high halides were passed down through the tube at a rate which gave a pressure in the tube of 1–5 Torr. However, the gas emerging from the nozzle at the end of the tube expanded rapidly into a vacuum better than 10^{-5} Torr and passed by a line-of-sight path to a liquid nitrogen-cooled surface. This apparatus is, of course, equally suitable for preparing the longer lived species like SiF_2 (see p. 153).

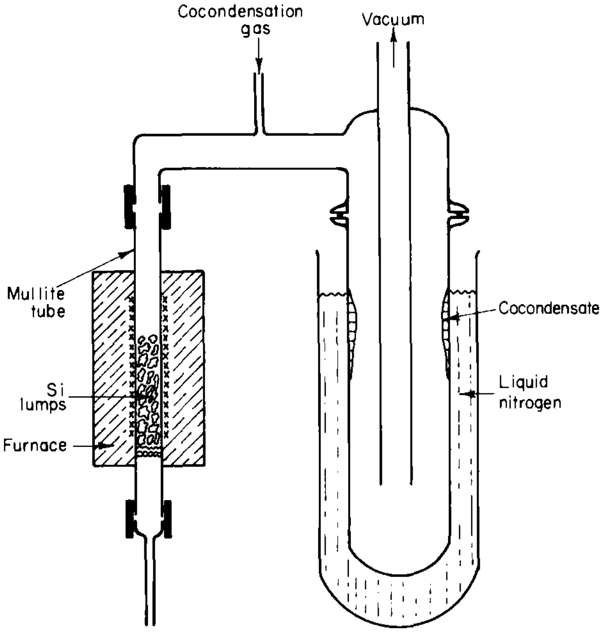


FIG. 5. Apparatus for cocondensing SiF_2 and volatile compounds.

Figure 7 shows the type of apparatus used by Skell and Cholod (*89*) for pyrolysis of chloroform at 1300° and condensation of the resulting

CCl_2 in solutions of alkenes in low-melting alkanes at about −120°. The graphite pyrolysis tube was heated by simply passing a current through it.

Atomic hydrogen has been formed by Klein and Scheer (*46*) and other workers (*35*) by thermal decomposition of H_2 on a heated tungsten ribbon mounted in the center of a flask cooled by liquid nitrogen. The walls of the flask were coated with a condensed layer of a compound which might react with the hydrogen atoms. With a hydrogen pressure of 0.05–1.0 Torr, atomic hydrogen formed on the filament diffused rapidly to the walls.

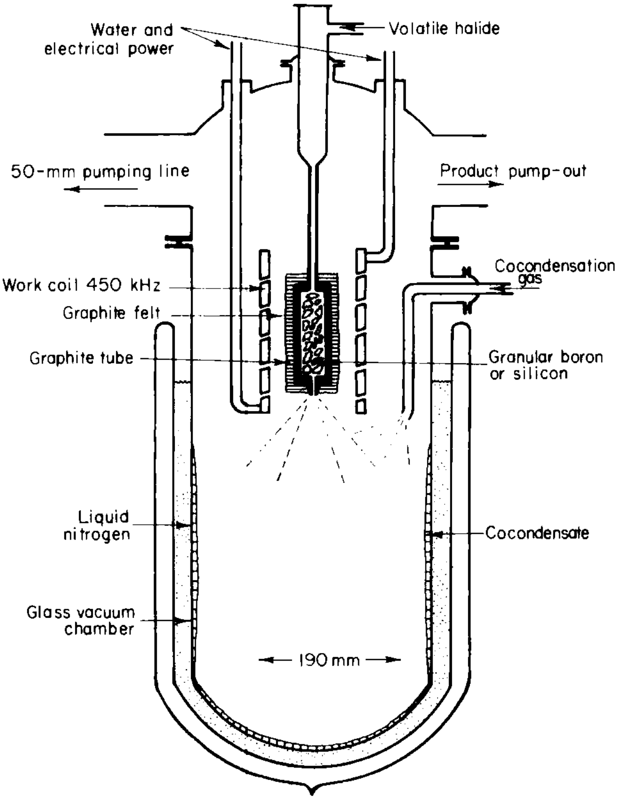


FIG. 6. Apparatus for studying reactions of short-lived boron or silicon subhalides.

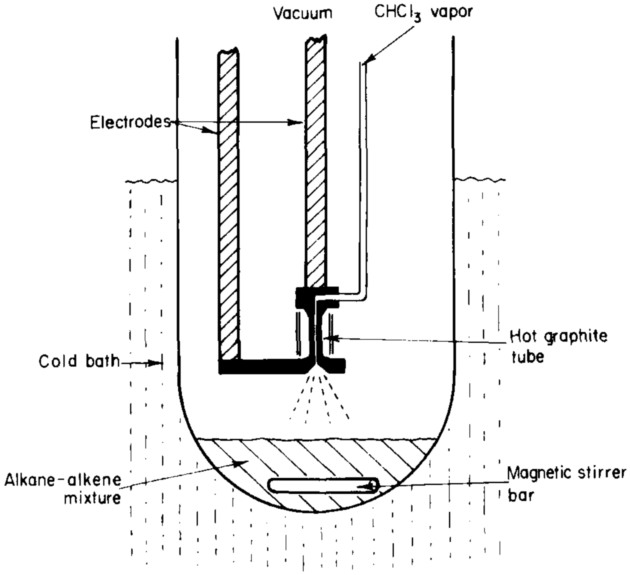


FIG. 7. Apparatus for condensation of CCl_2 in a cold alkane–alkene mixture. After Skell and Cholod (*89*).

B. CONDENSATION PROCEDURES

As can be seen from Figs. 2, 3, 4, and 6, the most common way of creating a cold surface on which the high temperature species can condense is by immersing part of the vacuum chamber in liquid nitrogen. This provides the largest possible cold area which is important for a number of reasons.

The surface acts as a cryogenic pump. The larger the cold area, the more quickly it pumps condensible vapors. It is then possible to pass relatively large amounts of vapors of compounds to be condensed with high temperature species, into the vacuum chamber without causing a large increase in pressure. For example, boron trichloride has been passed into the vacuum chamber shown in Fig. 2 at a rate of 3 moles/hr. During this process the pressure measured at the top of the pot was about 10^{-4} Torr. The speed of pumping of the diffusion pump assembly used to evacuate the reaction chamber is usually very low compared with the pumping speed of the cold surface for condensible vapors.

Heat is radiated to the cold surface from the source of the high temperature species. Removal of this heat is hindered by a thick layer of condensed material. The larger the surface, the thinner the deposit of condensed material and so the surface will be cooler and act as a more efficient pump. Large vacuum chambers with cooled walls a long way from the hot source are thus most desirable, although more difficult to construct and use than smaller ones. The problem has been solved in a different way in the rotating cryostat apparatus described by Mile (*65*). In the apparatus shown in Fig. 5, the cold surface is shielded from the hot source and a smaller area can be used effectively.

Various forms of inlet systems for the compounds to be condensed with the high temperature species have been used, as seen in Figs. 2–6. Their purpose is to distribute the vapor over the cold surface as uniformly as possible without allowing the vapor to impinge on the furnace. With liquid nitrogen as the coolant, it is not usually possible to condense compounds with boiling points lower than about −130° without seriously raising the pressure in the vacuum chamber.

Condensation of the high temperature species into a cooled liquid avoids the use of an inlet system. Two practical problems arise using this method. First, the high temperature species has to be sprayed downward into a pool of liquid. Downward evaporation of condensed phases is slightly more difficult to achieve than upward evaporation. Second, the liquid has to have a suitable vapor pressure at the temperature of condensation, preferably less than 10^{-5} Torr, although pressures as high as 10^{-3} Torr may be acceptable. On the credit side is the possibility of reacting an involatile material in solution with a high temperature species, and the potential to work on a much larger scale than with cocondensation.

C. RECOVERY OF REACTION PRODUCTS

Normal practice with the apparatus shown in Figs. 2–6 is to remove the liquid nitrogen coolant at the end of a run and allow the condensate to warm to room temperature with continuous pumping to remove excess reactants and volatile products. It has been found advantageous to use large bore pumping lines so that sparingly volatile products can be pumped out of the vacuum chambers fairly quickly. This is particularly important if the products are unstable.

Products that are not volatile are rather difficult to recover if they are spread in a thin layer over the inside of a vacuum chamber. Under these conditions deposition of the high temperature species and the compound with which it may react on a more restricted but accessible surface can be useful.

Characterization of the reaction products has mainly been carried out using conventional instrumental analytical methods.

IV. Reactions of High Temperature Species of Main Group Elements

High temperature species of use to synthetic chemists are unequally distributed among the main group elements. Species in Group III and IV, especially boron monofluoride, carbon vapor, and the silicon dihalides have been used most extensively and so appear to dominate this section. This situation may change in a few years as the chemistry of other species is explored.

A. GROUP I, II, AND III ELEMENTS

The high temperature species of the Group I, II, and III elements which have been used in synthesis are discussed under subheadings below.

The most important species of these elements as yet untried in synthetic experiments are the atoms of beryllium, aluminum, gallium, and indium. The gaseous monohalides of the Group II elements could be reactive, although difficult to form free of the vapors of the metals (*11*). The gaseous aluminum monohalides have been tried in cocondensation experiments by the author and by Ehlert (*24*), but no reactions has been observed with inorganic or organic compounds. Among species containing the elements in normal valencies, the gaseous hydroxides KOH, RbOH, and CsOH (*14*) and some halides, like AlF_3, seem potentially useful.

1. *The Group I and II Metals*

With the exception of beryllium, the Group I and II metals can be vaporized at temperatures much below 1000° under vacuum and they are strictly not high temperature species within the definition used in this chapter. The gaseous atoms appear to be highly reactive in condensation reactions at low temperatures, but they have been little used by synthetic chemists. This is mainly because the reactivity of the atoms at low temperatures is not very much greater than that of the metals used under conventional conditions. Skell (*88*) has reported that magnesium atoms react on condensation with alkyl halides to give alkylmagnesium halides. Klabunde *et al.* (*45a*) have recently described reactions of zinc atoms with perfluoroalkyl iodides. Group I metals have also been reacted with organic compounds at low temperatures, although the objectives of the experiments have generally been to obtain spectra of the radicals formed (*65*). Andrews and Pimentel (*4*) and Andrews and Carver (*3*, *17*) have studied reactions of lithium atoms with halocarbons and oxygen in noble gas matrices at 20°–50°K by infrared spectroscopy.

2. *Boron Atoms*

Boron has been vaporized by electron bombardment heating of a boron rod in an apparatus like that shown in Fig. 3 (*120*). The vapor species was believed to be monatomic boron in a ^2P electronic state. The boron vapor was condensed with BF_3, BCl_3, PCl_3, HCl, HBr, NH_3, C_6H_6, and CO_2 at −196°, and in each case reaction was observed. Carbon dioxide was reduced explosively to carbon monoxide when the cocondensate was warmed to about −150°. The boron and phosphorus trihalides each gave

$$B(g) + CO_2(g) \xrightarrow[\text{warm to } -150^\circ]{\text{cocondense } -196^\circ} \frac{1}{n}(BO)_n + CO \tag{9}$$

a small yield, based on the boron atoms condensed, of the corresponding catenated tetrahalides B_2F_4, B_2Cl_4, and P_2Cl_4; e.g.,

$$B(g) + PCl_3(g) \xrightarrow[\text{warm to } 25^\circ]{\text{cocondense } -196^\circ} BCl_3 + P_2Cl_4\ (10\%\ \text{yield}) + \text{involatile polymer} \tag{10}$$

The boron atoms caused complete polymerization of benzene. Since boron atoms are an odd-electron species, they must form free radicals in initial reactions with other compounds which would promote the polymerization of many reactants. For this reason, boron atoms are not very useful in chemical synthesis.

3. *Boron Monofluoride and Monochloride*

Boron monofluoride is the easiest of the known boron subhalide species to make at high temperatures. It has been formed in high yield by passing BF_3 over boron at 2000° (*119*) in an apparatus like that shown in Fig. 6. Its chemistry has proved very rich and can be considered in two parts.

a. Reactions of BF with Inorganic Compounds. When gaseous BF is condensed at −196° in the presence of a small amount of BF_3, a sequence

$$\begin{tikzcd} & & B_2F_4 \arrow[r, "BF"] & B_3F_5 \\ BF(g) \arrow[r, "\text{condense } -196^\circ"] & {} \arrow[ur, "BF_3"] \arrow[dr, "BF"'] & & \\ & & \text{slightly volatile B–F compounds containing 10–14 boron atoms} & \end{tikzcd} \tag{11}$$

of reactions occurs which is shown in Eq. (11). Cocondensation of BF and B_2F_4 gives much improved yields of B_3F_5. This last compound is very unstable at temperatures above −50° and quickly disproportionates.

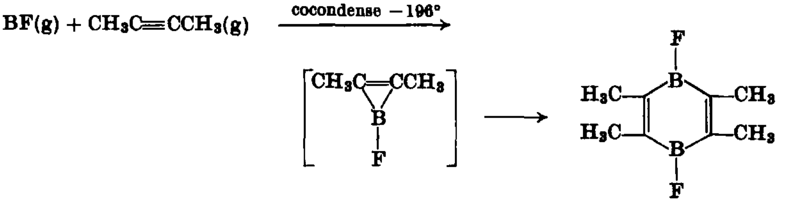
$$4B_3F_5 \longrightarrow B_8F_{12} + 2B_2F_4 \tag{12}$$

The compound B_8F_{12} is a bright yellow, volatile oil which decomposes above −10°. The most important property of the compound is its ability to react with "soft" bases (*71*) to form stable crystalline solids of general formula $(BF_2)_3BX$, where X is a molecule of the base. Complexes have been formed with CO, PF_3, PCl_3, PH_3, AsH_3, and $(CH_3)_2S$ (*43*, *119*). The structure of the complex with PF_3 was shown by X-ray crystallography to contain a tetrahedral arrangement of three BF_2 groups and the PF_3 molecule around a central boron atom (*20*). The complexes can also be made by cocondensation of BF and the base at −196°, although this synthesis must clearly involve complex reactions on the cold surface.

There is still some uncertainty about the structure of B_8F_{12} and the higher boron fluorides formed in the polymerization of BF on a cold surface. All spectroscopic evidence suggests that the compounds contain only $>B{-}BF_2$ groups and no BF groups, in contrast to the higher boron chlorides which are definitely composed of BCl groups (*61*).

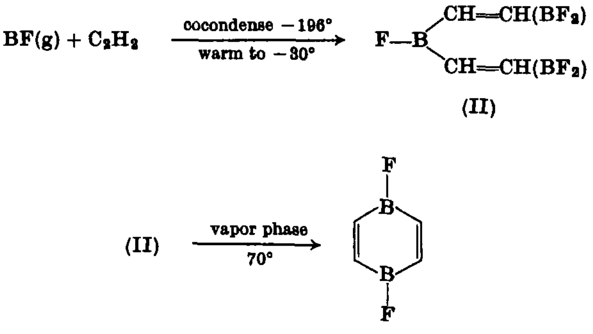
The use of BF as a reagent in low temperature condensation reactions is presently the only way known for making the higher boron fluorides. Electrical discharge methods which work well for the higher boron chlorides do not work for boron fluorides (*61*).

b. Reactions of BF with Organic Compounds. Cocondensation of 2-butyne and BF gives fairly good yields of the 1,4-diboracyclohexadiene derivative (I) (*124*). This may be formed by a two-step process on the cold surface. However, the reaction between BF and acetylene on cocondensation was found to be more complex. It is not clear how (II)



(I)

(13)



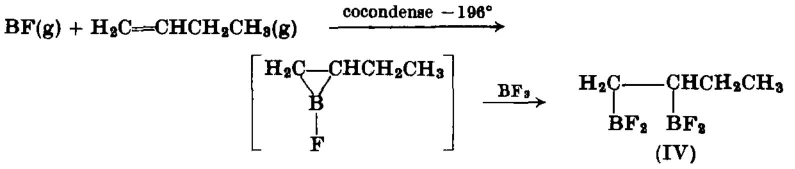
(II)

(14)

(III)

was formed and whether or not an analog of (II) was a short-lived intermediate in the formation of (I). These reactions of BF (or BCl) with acetylenes are the only known way of making the 1,4-diboracyclohexadiene ring system, other methods yield *clovo*-carborane structures.

Condensation of BF with 1-butene gave good yields of (IV) (*43*),



(IV)

(15)

perhaps by the steps shown in Eq. (15). The same compound can be made by heating 1-butene with B_2F_4 at about 100°, but the mechanism of the reaction is probably different from that in Eq. (15).

c. Boron Monochloride. The formation of BCl from BCl_3 and boron requires temperatures appreciably above 2000°, beyond the eutectic point for graphite and boron. Thus, the graphite furnace shown in Fig. 6 cannot be used and the experimental problem of making BCl efficiently by this route has not been solved.

It has been found that thermal cracking of diboron tetrachloride at 1100° at 0.1–5.0 Torr pressure in a rapid flow system produces high yields of a mixture of BCl and BCl_3. The BCl has been trapped by reaction with acetylene to give 1,4-dichloro-1,4-diboracyclohexadiene, an analog of (III) (*54a*). Alternatively, BCl can be made when an electric discharge is struck in B_2Cl_4 (*61*) and then condensed with other compounds at −196° (*54a*).

4. Other Boron Species

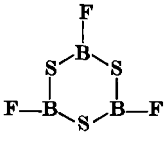
Boron monoxide gas, B_2O_2, is formed by heating a mixture of B_2O_3 and boron. It will condense on a surface at room temperature to form a brownish solid $(BO)_n$ (*40*). This solid is air- and moisture-sensitive, but otherwise less reactive than another polymer $(BO)_n$ made by dehydrating subboric acid. The latter polymer reacts with BCl_3 at 200° to give B_2Cl_4 in 25% yield (*52*). Recently it has been found that cocondensation of gaseous B_2O_2 and BCl_3 at −196° gives a 60% yield of B_2Cl_4 according to (16). This work (*128*) suggests that gaseous B_2O_2 is much more reactive

$$B_2O_2(g) + 4BCl_3 \xrightarrow{\text{cocondense}} 2B_2O_3 + 3B_2Cl_4 \qquad (16)$$

than the polymerized forms, although it is a "normal valency" compound (Section II).

The long-lived gaseous species HBS, formed from H_2S and boron at 1300° (*44*) has not been used with much success in low temperature reactions. Kirk (*43*) obtained slight evidence for a volatile complex $HBS \cdot NH_3$ resulting from the reaction of HBS and NH_3 at −196°.

The action of SF_6 on boron at 1300° forms a gaseous compound $(FBS)_2$ which has a lifetime comparable to that of silicon difluoride (Section II, B) in the gas phase. The compound polymerizes to involatile solids at room temperature, but if condensed at −196° and then allowed to warm to room temperature, good yields of the cyclic trimer (V) are formed (*43*).



(V)

B. SPECIES CONTAINING CARBON

The most important carbon-containing high temperature species in synthetic work are those present in carbon vapor. Much of the work with carbon vapor has been performed by Skell and his associates and is pure organic chemistry. Nevertheless, the work is central to the theme of this chapter as it represents the most detailed study of a series of condensation reactions which has yet been made.

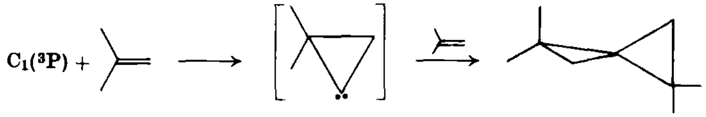
1. *Reactions of Carbon Vapor Species*

a. The Composition of the Vapor. The vapor species over hot carbon have been investigated mass spectrometrically by Drowart *et al.* (*23*) and shown to include C_1, C_2, C_3, C_4, and higher polymers. When formed under high vacuum in an arc the vapor composition does not correspond to that predicted from thermal equilibrium studies such as those of Thorn and Winslow (*118*). Data obtained from cocondensation experiments when carbon was vaporized from a 16-V arc, suggest an approximate composition C_1 40%, C_2 28%, C_3 <25%, C_4 2%, plus higher polymers (*29, 96, 97, 103*).

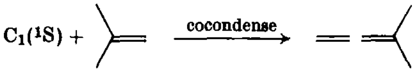
Vaporization from an arc also produces excited electronic states of all the species present. Skell and Engel (*90, 91*) claim that C_1 is formed in its ^3P ground state, but also in excited singlet states, ^1D and ^1S, lying 39 and 60 kcal, respectively, in energy above the ground state. The excited ^1S state probably accounts for the bulk of the C_1 formed, but it decays rapidly with a half-life of about 2 sec, on the cold surface.

Evidence for the existence of these states has been obtained by observing the changes in reactivity with time of alkane matrices of the carbon species at −196° toward olefins and other organic compounds. The C_2 and C_3 species are believed to be formed in both excited triplet and ground singlet electronic states (*103*, *104*, *107*).

b. Reactions with Organic Compounds. Three types of reactions have been found between olefins and different carbon species. The reaction of C_1 in its ^3P ground state forms spiropentanes. The ^3P state was obtained by trapping carbon vapor in neopentane and allowing the excited states to decay to the ground state before adding an olefin (*91*). Thus, with isobutene a spiropentane is formed via a carbene intermediate. The reaction is represented in Eq. (17) showing only the carbon skeleton. The excited ^1S state forms allenic compounds. Cocondensation of isobutene and carbon vapor on a surface at −196° gave 3-methyl-1,2-butadiene in a yield corresponding to about 40% of the evaporated carbon (*93*). The cocondensation procedure lends itself to work on a much larger scale than the aging technique used to study the ^3P state and it is much more convenient. As a consequence, carbon atom reactions provide a practical synthesis of some allenic compounds but not of spiropentanes. McGlinchey *et al.* (*54*) have reported that cocondensation reactions of fluoroolefins with carbon vapor form mainly allenic compounds. Perfluorobut-1,2-diene was obtained in 20% yield based on the carbon evaporated, from perfluoropropene.



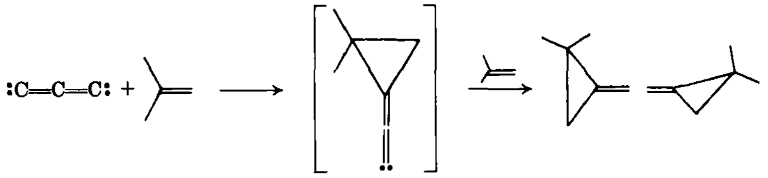
(17)



(18)

$$C(^1S)? + CF_3CF{=}CF_2 \xrightarrow{\text{cocondense}} CF_3CF{=}C{=}CF_2 \qquad (19)$$

The C_3 molecule adds to olefins to form a class of compounds which had not previously been made, the bisethanoallenes. The reaction with isobutene is shown schematically in Eq. (20). Skell *et al.* (*107*) report that the stereochemistry of the products is affected by aging of the carbon vapor deposited in alkane matrices, and they have interpreted this on the basis of initial deposition of a short-lived triplet state of C_3.


(20)

Sprung *et al.* found that cycloheptatriene and toluene were the main volatile products when carbon vapor was condensed on top of a layer of benzene at −196°. The vapor was formed in tiny amounts from a resistance heated graphite rod. The methyl group in the toluene was presumably formed by hydrogen abstraction by an initial reaction product. Hydrogen abstraction reactions giving methyl groups or free C_2 and C_4 hydrocarbons have also been reported by Skell and his associates (*29*, *95*, *103*, *105*) in work with carbon vapor.

Only the excited ^1S state of C_1 reacts with alkanes. Insertion occurs into C–H bonds fairly randomly, so that secondary reactions of the resulting carbenes cause many products to be formed (*92*). Neopentane is inert and has been much used by Skell and his associates for isolating carbon species.

Organic compounds containing oxygen are often deoxygenated by C_1 (^1S) with the formation of carbenes and carbon monoxide (*73*, *97*, *98*, *100*, *101*, *102*). With alcohols dialkoxymethanes are formed from C_1 species.

$$C_1 + 2CH_3OH \xrightarrow{\text{cocondense}} (CH_3O)_2CH_2 \tag{21}$$

A similar insertion occurs with C_3 species (*96*).

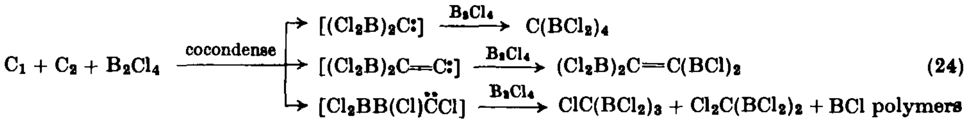
$$C_3 + 2ROH \xrightarrow{\text{cocondense}} (RO)_2CHC{\equiv}CH \tag{22}$$

Carbon vapor species do not dechlorinate organic chloro compounds, insertion into the C–Cl bonds by C_1 species seems to be the main reaction. As in other reactions with carbon vapor, cocondensation gives slightly different products than those obtained with aged carbon matrices. This is illustrated in Eq. (23) for the reaction with chloroform (*94*).

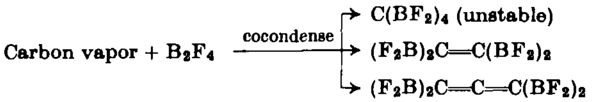
$$\begin{tikzcd}
C_1(^1S)? + CHCl_3 \arrow[r, "\text{cocondense}"] & {[Cl_2CH\ddot{C}Cl]} \arrow[r, "CHCl_3"] \arrow[d] & Cl_2CHCCl_2CHCl_2 \\
C_1(^1D, ^3P)? + CHCl_3 \arrow[r] & ClHC{=}CHCl &
\end{tikzcd} \tag{23}$$

c. Reactions with Inorganic and Organometallic Compounds. Attempts to introduce carbon into inorganic compounds by reactions with carbon vapor have been fairly successful and have established practical synthetic routes to some new compounds. The experiments have all been run under cocondensation conditions with no attempt to form aged matrices of carbon species in inert substrates, so that the excited electronic states of carbon must play a large part in the observed reactions.

Carbon vapor has been condensed with B_2Cl_4 and B_2F_4 at −196° and products resulting from insertion of carbon into both B–B and B–halogen bonds have been observed (*22*, *133*). As with reactions of organic compounds, carbene intermediates were probably formed.



$$C_1 + C_2 + B_2Cl_4 \xrightarrow{\text{cocondense}} \begin{cases} [(Cl_2B)_2C\colon] \xrightarrow{B_2Cl_4} C(BCl_2)_4 \\ [(Cl_2B)_2C{=}C\colon] \xrightarrow{B_2Cl_4} (Cl_2B)_2C{=}C(BCl)_2 \\ [Cl_2BB(Cl)\ddot{C}Cl] \xrightarrow{B_2Cl_4} ClC(BCl_2)_3 + Cl_2C(BCl_2)_2 + \text{BCl polymers} \end{cases} \qquad (24)$$



$$\text{Carbon vapor} + B_2F_4 \xrightarrow{\text{cocondense}} \begin{cases} C(BF_2)_4 \text{ (unstable)} \\ (F_2B)_2C{=}C(BF_2)_2 \\ (F_2B)_2C{=}C{=}C(BF_2)_2 \end{cases} \qquad (25)$$

No C_3 product was isolated in the reaction of carbon vapor and B_2Cl_4, but this may have been due to the low volatility of the higher chloro compounds. About 1.5 mmoles of the interesting product $C(BCl_2)_4$ were obtained per run involving the evaporation of 30 mmoles of carbon and its condensation with 150 mmoles of B_2Cl_4 over a period of 15 min (*133*).

Stone and his co-workers have found the reactions of carbon with BCl_3 (*133*), $GeCl_4$, and PCl_3 (*53*) to be basically similar. In each case the major products isolated contained one carbon atom,

$$\begin{aligned} &C_1 + BCl_3 \xrightarrow{\text{cocondense}} Cl_2C(BCl_2)_2 + ClC(BCl_2)_3 \\ &C_1 + GeCl_4 \longrightarrow Cl_3CGeCl_3 + Cl_2C(GeCl_3)_2 \qquad (26) \\ &C_1 + PCl_3 \longrightarrow Cl_3CPCl_2 + Cl_2C(PCl_2)_2 \end{aligned}$$

$$\begin{aligned} &C_2 + BCl_3 \xrightarrow{\text{cocondense}} Cl_2B(Cl)C{=}C(Cl)BCl_2 \\ &C_2 + GeCl_4 \longrightarrow Cl_3Ge(Cl)C{=}CCl_2 \text{ (low yield)} \qquad (27) \\ &C_2 + PCl_3 \longrightarrow Cl_2P(Cl)C{=}CCl_2 \text{ (low yield)} \end{aligned}$$

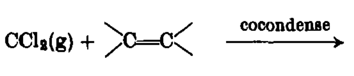
Binenboyn and Schaeffer (*8*) reported that the major product from the reaction of $SiCl_4$ and carbon vapor is the acetylenic compound $ClC{\equiv}CSiCl_3$. The formation of this would appear to involve insertion of a C_2 molecule into a Si–Cl bond. The difference between this result and that shown for BCl_3, $GeCl_4$, and PCl_3 in Eqs. (26) and (27), may stem from a real difference in the chemistry of the halides, but it is possible that the experimental conditions employed by the two sets of workers caused the difference. As was discussed in Section II, the relative rates of competing reactions can be affected by the surface temperature in the condensation which is influenced by the size of reactor and the power dissipated.

A simple insertion of C_1 into a B–C bond probably accounted for the formation of $(CH_3)_2C(BCl_2)_2$ from carbon and methyldichloroborane (*22*). Similarly the formation of thiophosgene from S_2Cl_2 and carbon vapor may have been the result of C_1 insertion into S–S or S–Cl bonds (*53*).

Condensation of carbon vapor with the less stable hydrides raises serious experimental difficulties. Hydrogen may be evolved during the codeposition which increases the pressure, allowing collisions in the gas phase. Schaeffer and his co-workers have attempted reactions of carbon vapor with B_5H_9 (*75*) and SiH_4 (*8*). From the former they isolated a small amount of a carborane, B_5CH_7. With the latter, hydrogen evolution caused organic compounds like benzene and acetylene to be formed in greater abundance than silicon-containing products.

2. Other Species Containing Carbon

a. Dichlorocarbene. Westcott and Skell (*137*) reported the formation of CCl_2 by pyrolysis of chloroform or carbon tetrachloride at about 1500° under high vacuum conditions, which allowed the CCl_2 to be condensed with other compounds on a cold surface. They showed, for example, that CCl_2 added to olefins to form 1,1′-dichlorocyclopropanes. The work was extended by Skell and Cholod (*89*), who sprayed the CCl_2 gas into a cooled, well-stirred solution of an olefin in an alkane (Fig. 7). The carbene reacted efficiently with the olefin under these conditions. However, the conclusion from the work with CCl_2 was that the compound formed at high temperatures reacted in the same way as the carbene liberated chemically at ordinary temperatures, e.g., from the decomposition of $LiCCl_3$ (*66*). Thus, as mentioned for CF_2 (Section II), there is little point in making CCl_2 at high temperatures.



(28)

b. Carbon Monosulfide. The chemistry of CS is little known. It can be formed by decomposition of CS_2 on metal surfaces at 1700° (*9*) or from metal sulfides and carbon at high temperatures (*138*). Solan (*109*) has found that CS appears to be reactive at low temperatures, and it seems likely that a careful study of this species would be rewarding.

C. SPECIES CONTAINING SILICON

1. *Silicon Atoms*

The vapor of silicon contains a much smaller proportion of polymers than the vapor of carbon, and Si_1 is the dominant species at low pressures (*33*).

Skell and Owen (*99*) vaporized silicon from a resistively heated silicon rod and condensed the vapor with trimethylsilane at −196°. The silicon atoms inserted into the Si–H bond and a trisilane was isolated in fair

$$\mathrm{Si(g) + (CH_3)_3SiH \xrightarrow{cocondense} [(CH_3)_3Si\ddot{Si}H] \xrightarrow{(CH_3)_3SiH} (CH_3)_3SiSiH_2Si(CH_3)_3} \qquad (29)$$

yield. This seems to be one of the few reactions of silicon atoms which give good yields of products. Kirk and Timms (*45*) vaporized silicon by electron bombardment of a silicon rod and condensed the vapor with BF_3, BCl_3, and B_2F_4. Almost no volatile products were obtained at all from the first two compounds, while the third formed the new compound $FSi(BF_2)_3$ in a 1% yield, presumably by reactions analogous to those of Eqs. (24) and (25). In each case, the main product was involatile polymeric material which contained only a small amount of elemental silicon. Other cocondensation experiments with silicon vapor have mainly failed to give volatile products, so that its future as a reagent is much less promising than that of carbon vapor.

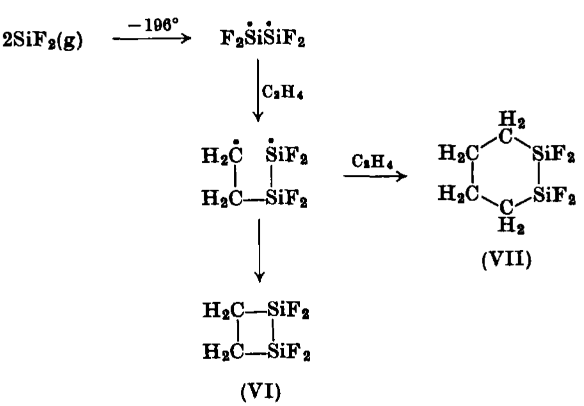
2. *Silicon Difluoride*

a. The Reactive Species. Silicon difluoride gas is easily prepared from SiF_4 and silicon at temperatures above 1100° under vacuum. It is also formed by thermal decomposition of Si_2F_6 at low pressures (*81*). It reacts with a wide range of compounds on condensation at −196°. However, its long lifetime in the gas phase is scarcely affected by the presence of the vapors of several of the compounds with which it will react at −196° (*130*). It exhibits the unusual behavior of being more reactive in the condensed phase at low temperatures than in the gas phase at ordinary temperatures.

A characteristic of many low temperature reactions of SiF_2 is the formation of products containing two or more silicon atoms, often with no product containing only one silicon atom. These observations suggested that in the polymerization of SiF_2 at low temperatures, the simple polymers Si_2F_4, Si_3F_6, etc., are more reactive than monomeric SiF_2. Evidence to support this view was obtained from the infrared spectra of the polymerization of SiF_2 in noble gas matrices (*6*). The high reactivity of these simple polymers indicated that they are diradical rather than olefinic species, and a further proof of this came from electron spin resonance studies of the polymerization at −196° (*34*).

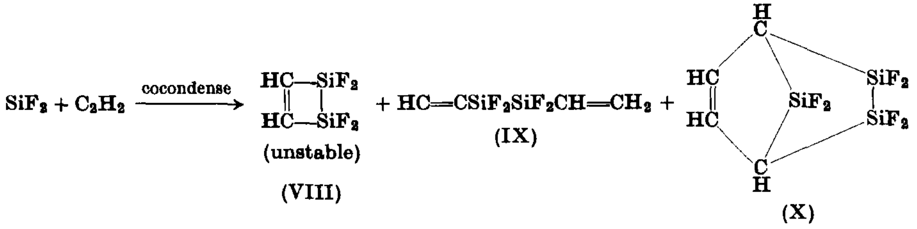
Cocondensation reactions of SiF_2 with compounds capable of breaking the Si–Si bonds in polymers or inhibiting their formation, give products containing one silicon atom. Sometimes the yields in these reactions are much higher than in those which depend on the formation of the diradical polymers.

b. Reactions with Unsaturated Organic Compounds. Cocondensation of SiF_2 and ethylene at −196° gave small yields of the two cyclic volatile products (VI) and (VII) (*115*).



(30)

The reaction with acetylene was found to be more complicated and several products have been obtained containing Si–Si bonds. The low

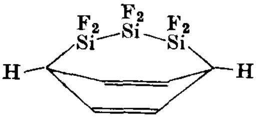


(31)

stability of (VIII) may be due to ring strain. The mechanism for the formation of (IX) and (X) is not known (*117*).

The reaction of benzene and SiF_2 produced another unexpected bicyclic ring compound (XI) (*131*). Mass spectrometric evidence was obtained for a homologous series $C_6H_6(SiF_2)_n$, where $n = 2$ to at least

6, perhaps all with silicon chains bridged across the 1,4-positions of a cyclohexadiene ring.



(XI)

Cocondensation of SiF_2 and hexafluorobenzene at −196° gave a different type of reaction. As the condensate warmed to room temperature it emitted flashes of light (*131*). The products isolated were $C_6F_5SiF_3$ and mixed isomers of $C_6F_4(SiF_3)_2$, but no compounds containing Si–Si bonds. It seems quite possible in this case that the initial reaction products were of the same type as formed with benzene, but that on warming an exothermic transfer of fluorine from carbon to silicon occurred with destruction of the Si–Si bond system. Partially fluorinated aromatic and olefinic compounds show this same effect (*115, 131*).

c. ***Reactions with Inorganic Compounds***. One of the most thoroughly studied reactions of SiF_2 is that with BF_3 at low temperatures. Using the apparatus of Fig. 5, the products were $SiF_3SiF_2BF_2$, $SiF_3(SiF_2)_2BF_2$, and much smaller amounts of higher homologs in the series $SiF_3(SiF_2)_nBF_2$ (*129*). The compound SiF_3BF_2 was not formed in the reaction. When SiF_2 and BF_3 were simultaneously isolated in a krypton matrix at 20°K, it was shown by infrared spectroscopy that $SiF_3SiF_2BF_2$ was first formed on warming the matrix to 35°K. This was the same temperature at which new bands appeared in the infrared spectrum of matrix-isolated SiF_2, tentatively assigned to the diradical species Si_2F_4 (*6*).

It has been found recently that when SiF_4 at 1–5 Torr pressure is passed over silicon or silicon carbide heated to 1200°–1800° in the apparatus of Fig. 6, and the resulting gases are condensed with BF_3 at −196°, SiF_3BF_2 is formed in addition to the expected $Si_2F_5BF_2$ and $Si_3F_7BF_2$. It is thought that SiF_3BF_2 must be formed by a reaction of a hitherto undetected, short-lived high temperature species, perhaps triplet SiF_2 (*108a*).

In another experiment involving the Si–B–F system, SiF_4 was passed over boron at 1800° in the apparatus described in Fig. 6. The gas issuing from the graphite tube was believed to contain a mixture of SiF_2, BF, and BF_3 (*45*). On condensing this mixture at −196° the main volatile product which could be isolated was $F_2Si(BF_2)_2$.

$$SiF_2(g) + BF(g) \xrightarrow{\text{cocondense } -196°} [F_2\dot{S}i\dot{B}F]? \xrightarrow{BF_3} F_2Si(BF_2)_2 \qquad (32)$$

Silicon difluoride reacts with most halides except SiF_4, when condensed with them at low temperatures. Sometimes the products are not stable, e.g., reactions with GeF_4, NF_3, PF_3, and SF_4 (*60*), generally due to halogen abstraction by the silicon. The reaction with CF_3I occurs smoothly, but gives a large range of products (*58*). Free halogens react

$$\begin{gathered}SiF_2(g) + CF_3I \xrightarrow{\text{cocondense}} CF_3SiF_2I \text{ (main product)} + \\ CF_3SiF_2SiF_2I + SiF_3I + SiF_2I_2 + SiF_2ISiF_2I + SiF_3SiF_2SiF_2I + SiF_2ISiF_2SiF_2I\end{gathered} \tag{33}$$

quantitatively with SiF_2 in the gas phase or on condensation at low temperatures, and the reaction of SiF_2 and I_2 is the best method for making SiF_2I_2 (*57*).

Oxygen reacts with gaseous SiF_2 at room temperature with emission of a bright blue glow. It was found that SiF_2 could be deposited in a matrix containing 50% O_2 and 50% Kr at 20°K without reaction. Only on warming to 45°–50°K was any reaction detected using the infrared spectrum. Thus, paradoxically, SiF_2 is less reactive toward O_2 than BF_3 at very low temperatures, although the situation is quite reversed at room temperature. The final product of the reaction of SiF_2 with most oxygen-containing compounds is a complex mixture of silicon oxyfluorides (*7*, *116*). The steps in the reactions with NO and CO have been followed by infrared spectroscopy in krypton matrices at 20°–60°K (*6*).

Reactions of SiF_2 with inorganic hydrides give well-defined products. Germane forms $HSiF_2GeH_3$, together with smaller amounts of $HSiF_2SiF_2GeH_3$ and less stable higher homologs (*110*). Similarly, H_2S forms $HSiF_2SH$, a little of the unstable $HSiF_2SiF_2SH$, and the corresponding S–S-bonded compounds $HSiF_2SSH$ and $HSiF_2SiF_2SSH$ (*84*). Water and SiF_2 give good yields of $HSiF_2OSiF_2H$ (*59*).

Many of the compounds described above, formed from reactions of SiF_2 with both organic and inorganic compounds, are very difficult or impossible to make except by using SiF_2 as a reagent. The compound has an assured place among important synthetic reagents in silicon chemistry, particularly as it is long-lived as a gas and easy to make.

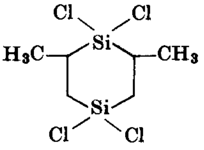
3. *Silicon Dichloride and Silicon Dibromide*

Monomeric $SiCl_2$ is formed from $SiCl_4$ and silicon at about 1300° under low pressure, but it is quickly converted to polymers or perchlorosilanes by collisions with the walls of the reaction vessel or with other molecules (Section II,B). Its chemistry is as much akin to that of CCl_2 as to SiF_2. The compound behaves like other carbene analogs such as $Si(CH_3)_2$ or GeI_2 (*68*).

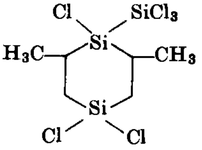
Cocondensation of $SiCl_2$ and olefins at −196° gives high yields of

1,4-disilacyclohexane derivatives. With propene, (XII) is the main product, together with higher homologs such as (XIII), in which $SiCl_2$ has inserted into an Si–Cl bond in (XII). This insertion into Si–Cl bonds seems the most favored reaction of $SiCl_2$, and it is difficult to avoid the formation of compounds like (XII) even in the presence of excess propene (*108*).

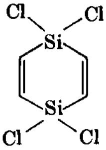
The reaction of $SiCl_2$ with acetylene is complex and gives a large amount of volatile polymer. The main volatile product is the 1,4-disilacyclohexadiene derivative (XIV), which is fairly unstable, but other compounds containing acetylenic groups are also formed. The reaction is still being investigated.



(XII)



(XIII)



(XIV)

In contrast to the reaction of SiF_2 and BF_3, cocondensation of $SiCl_2$ and BCl_3 forms $SiCl_3BCl_2$ in a 15% yield based on the $SiCl_2$. This is much superior to the electrical discharge synthesis of this compound reported by Massey and Urch (*62*). The reaction with PCl_3 gives a similar yield of $SiCl_3PCl_2$ (*122*), but the yield of $SiCl_3CCl_3$ from $SiCl_2$ and CCl_4 is lower. The conversion of M–Cl to M–$SiCl_3$ by a cocondensation reaction with $SiCl_2$ seems to be a fairly general and synthetically useful process.

Many carbenes can be formed by reactions at ordinary temperatures. This is not really possible for either SiF_2 or $SiCl_2$, but the latter is implicated as an intermediate in reactions of silicon with organic chloro compounds at temperatures of 100°–400° (*27*).

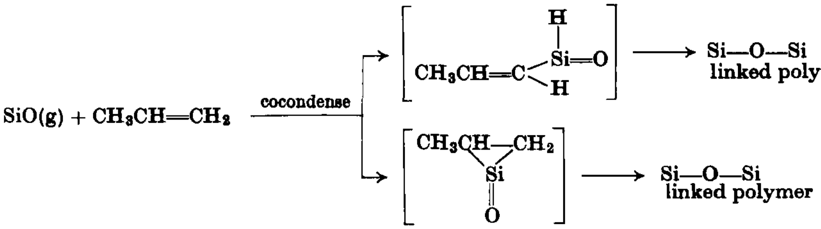
Silicon dibromide has been formed from $SiBr_4$ and silicon under very similar conditions to those used for $SiCl_2$. It appears to be as short-lived as $SiCl_2$ and readily forms polymers and perbromosilanes. Very little of its chemistry has been studied, but there is every reason to suppose it will be like that of $SiCl_2$.

Silicon diiodide cannot be made under high vacuum conditions from silicon and SiI_4 because of dissociation to silicon and iodine atoms (*79*).

4. *Silicon Monoxide and Other Species*

Gaseous silicon monoxide is easily formed by heating mixtures of silicon and silica above 1300° under vacuum. The polymerization of SiO in noble gas matrices has been studied by two groups of workers (*1*, *30*), and has been shown to involve the formation of oxygen linked polymers Si_2O_2, Si_3O_3, etc.

Silicon monoxide has been found to react with most unsaturated organic compounds on cocondensation at −196° (*80*). In every case the products were infusible solids. For example, the reaction with propene yielded a transparent solid of approximate composition $C_3H_6(SiO)_3$, which seems to have been formed by attack of SiO and its polymers on propene in two ways. Benzene and SiO formed a white solid $C_6H_6(SiO)_4$. This also appears to have involved insertion of SiO into C–H bonds and attack on the aromatic system to form a derivative of 1,4-cyclohexadiene, as hydrolysis yielded benzene and 1,4-cyclohexadiene. The relative reactivities of monomeric and simple polymeric forms of SiO are not known, but it is possible that the polymers are the more active species which would account for the composition of the above products.



(34)

Silicon monosulfide was reported to react with various inorganic halides at −196° to form new volatile products, but details have not yet been published (*56*).

Vaporization of silicon carbide is said to yield the gaseous species SiC_2, Si_2C, and SiC, in addition to a larger amount of silicon vapor (*135*). Mixed B–C–Si and B–Si species were also detected. The cocondensation chemistry of these mixed species could prove very interesting.

D. Species Containing Other Main Group Elements

1. *Germanium and Tin Atoms and Compounds*

Both germanium and tin are fairly easily vaporized to give mainly atoms with some polymers (*86*). No work has been published on cocondensation reactions of these elements, but some preliminary studies have been made (*64*). These indicate that germanium vapor behaves like silicon vapor, reacting with many compounds at low temperatures, but not forming simple, volatile products. Tin vapor has been successfully reacted with some alkyl halides to give alkyltin halides at low temperatures.

Gaseous germanium dihalides are not true high temperature species as they can be formed from the tetrahalides and germanium at 200°–400°. Germanium difluoride vapor contains polymeric species (*143*), but the dichloride and dibromide are monomeric (*134*). None of these species seems to be reactive in cocondensation reactions at −196°. However, solid $GeCl_2$, $GeBr_2$, and GeI_2 show some carbenoid properties in reactions with organic compounds at 25°–300° (*68*, *123*).

Germanium and tin monoxides are formed as vapour species at temperatures of 700°–1000° from the elements and their dioxides. Matrix isolation infrared studies on GeO and SnO have shown that their polymerization is similar to that of SiO (*2*). No cocondensation reactions have been attempted with the species, but there is a reasonable chance that they will prove reactive and form products similar to those from silicon monoxide.

2. *Group V, VI, and VII Elements and Hydrogen*

The vapors of phosphorus, arsenic, sulfur, and selenium are complex below 1000°, but at higher temperatures diatomic species predominate (*86*). The diatomic species P_2, As_2, S_2, and Se_2 are energetic compared with the normal forms of the elements, but their use as reagents in cocondensation reactions is of uncertain value. Unlike C_2, they contain elements in formally stable valency states, unstable only with respect to the polymerized, single bonded P_4, As_4, S_8, and Se_8, respectively. They fall in the general class of species discussed in Section II,B. Similar comments apply to the mixed species containing these elements like gaseous PN (*16*).

The atomic species, P, As, S, and Se, are of much greater potential interest as reagents, but they are not easily made free of the diatomic species by high temperature methods. The atoms can be made more successfully by photochemical reactions (Section VI,A).

The species PF_2, possibly mixed with PF, was made by thermal dissociation of P_2F_4 at 800°–1000° under vacuum (*109*, *111*). Condensation of the gas at −196° formed small amounts of a new compound $P(PF_2)_3$. Attempts to react PF_2 with organic compounds at −196° gave no stable products.

The great majority of studies of synthetic reactions of atoms of nitrogen, oxygen, hydrogen, and the halogens have used methods such as discharges and photolysis which are outside the main scope of this chapter (see Section VI,A). The work of Klein and Scheer (*46*) on the mechanism of reactions of hydrogen atoms with olefins at −196°, in which the hydrogen atoms were formed on a hot filament, is an exception. Their method would seem to have potential for the synthesis of some inorganic compounds.

V. Reactions of High Temperature Species of Transition Elements

A. SPECIES OF INTEREST

1. The Metal Vapors

The transition metals vaporize mainly as monomeric species (*86*). Dimers such as Ni_2 have been seen by mass spectrometry (*41*), but as the metal–metal bond energies are fairly low compared with the heat of vaporization, these species form a tiny proportion of the vapor under low pressure evaporation conditions.

As discussed in Section II, A, vaporization of the first-row elements generally occurs at lower temperatures than for the second- and third-row elements. This is particularly true in the middle of the transition metal series where the binding energy of atoms in the solid lattice is extremely high for the second- and third-row elements. The metals Nb, Ta, Mo, W, Re, Os, and Ir, all require temperatures in excess of 2500° for appreciable vaporization, so their vapors are unlikely to be used in large-scale chemical synthesis. On the other hand, elements such as Cu, Ag, and Mn can be vaporized easily at rates as high as 1 mole/hr in laboratory apparatus (Fig. 2).

The synthetic uses of transition metal atoms fall into two classes (*125a*). The most obvious is the formation of complexes by condensation reactions with ligands at low temperatures. These will generally give products in which the metal is in a zero or other low valency state. As Pearson has pointed out (*71*), free transition metal atoms must be classed as "soft" acids and will be expected to combine readily with "soft" bases such as phosphines, CO, NO, and many unsaturated organic compounds. The other use of transition metal vapors in cocondensation syntheses is as dehalogenating agents. The thermodynamics of dehalogenation reactions of copper atoms compared with sodium atoms were discussed in Section II, A, and it was seen that the transition metal atoms are potentially powerful reagents. Their ability to form complexes imparts a degree of selectivity to some of their dehalogenation reactions not found with other metals and compounds.

2. Molecular Species

The use of high temperature molecular species of the transition metal elements as reagents in chemical synthesis is as yet entirely unexplored. The most promising species would appear to be those containing the elements in low valency states. However, it seems to be difficult to make most of the simple species known to spectroscopists free of other species such as the metal vapors (*19*, *42*). A possible exception is the monohalides of the rare earth elements (*142*).

Species such as gaseous TiO, VF_2, and CrF_2, which are formed from condensed phases at temperatures well above 1000°, may form a range of complexes on condensation with ligands which are not accessible from reactions of these compounds at ordinary temperatures. The particular case of ZrO_2 vapor was discussed in Section II,B. The technique of low temperature condensation might also be applied usefully to reactions of vapors of CuCl and AgCl and other species which are formed in the temperature range 500°–1000°.

B. Reactions of Metal Vapors with Inorganic Ligands

1. *Trifluorophosphine*

Condensation of transition metal vapors with trifluorophosphine at −196° has been shown to be a useful way of making the zero-valent PF_3 complexes in high yields (*127*). On a laboratory scale, the method is an attractive alternative to the normal high pressure routes to PF_3 complexes (*48*).

The reactions which have been studied are shown schematically in Eq. (35). In each case the metal vapor was condensed with PF_3 in at least a 1:8 mole ratio using an apparatus similar to that of Fig. 2. The approximate yields of products based on the metal vaporized, are shown in parentheses.

$$\mathrm{Cr(g) + PF_3(g)} \xrightarrow{\text{cocondense}} \underset{(65\%)}{\mathrm{Cr(PF_3)_6}} \tag{35}$$

Mn: no volatile product

Fe: $Fe(PF_3)_5$ (25%) + $(PF_3)_3Fe(PF_2)_2Fe(PF_3)_3$ (25%)

Co: $[Co(PF_3)_4]_x$ (50%)

Ni: $Ni(PF_3)_4$ (85–100%)

Cu: no volatile product

Pd: $Pd(PF_3)_4$ (70%)

The reaction of nickel with PF_3 is particularly efficient. The pressure in the vacuum system during codeposition of nickel vapor and PF_3 was always exceptionally low apparently due to "gettering" of the PF_3 by nickel atoms either in the gas phase or on the surface. The only other metal which showed this effect to the same extent was copper vapor. It is possible that a molecule such as $Cu–PF_3$ was formed in the gas phase or on the cold surface, but that it decomposed on warming to metallic copper and PF_3.

The reaction of iron vapor with PF_3 is very complicated. The relative amounts of the two products shown in Eq. (35) have been found to vary substantially with changes either in the temperature of the cold surface or in the ratio of Fe:PF_3 cocondensed. Other less stable products are also formed in small amounts, one of which may be $(PF_3)_3FePF_2Fe(PF_3)_3$ (*87*).

The failure to form any volatile product in the reaction of manganese and PF_3 is further proof (*48*) that the compound $(PF_3)_5MnMn(PF_3)_5$, analogous to $(CO)_5MnMn(CO)_5$, cannot be stable at room temperature. However, a slow evolution of PF_3 on warming the cocondensate from −196° indicated that some reaction had occurred at the low temperature.

The work represented by Eq. (35) demonstrated that PF_3 is an effective ligand in low temperature reactions with metal atoms. The products were conveniently volatile and easily separated from involatile solids left on the cold surface. Carbon monoxide is very similar in its properties as a ligand to PF_3, but it could not be used in these reactions because of its high vapor pressure at −196°. As a result, PF_3 has been chosen as the best ligand to use in conjunction with other ligands in some of the reactions described below.

Cocondensation of nickel vapor and PF_2Cl gave fair yields of $Ni(PF_2Cl)_4$ (*127*), but other metals gave no volatile products.

2. PH_3, *NO, and Ligand Precursors*

Few complexes of phosphine, PH_3, with transition metals have been reported. Condensation of nickel vapor with PH_3 at −196° was accompanied by hydrogen evolution, and more hydrogen was evolved when the condensate was allowed to warm to room temperature. No volatile product containing nickel was obtained, suggesting that $Ni(PH_3)_4$ is very unstable. An equimolar mixture of PH_3 and PF_3 condensed with nickel at −196° formed two new volatile compounds $Ni(PF_3)_2(PH_3)_2$ and $Ni(PF_3)_3PH_3$, which were separated from $Ni(PF_3)_4$ by low temperature distillation (*127*). Some hydrogen was also evolved when the condensate was warmed from −196°. The compound $Ni(PF_3)_2(PH_3)_2$ decomposed slowly above 0° evolving hydrogen. When allowed to warm to room temperature in the presence of PF_3, it was converted quantitatively to $Ni(PF_3)_3PH_3$.

The above reactions illustrate an important principle in synthesis at low temperatures. It seems likely that the ligands added randomly to the metal atoms on the cold surface in a diffusion-controlled process. Displacement of the weaker ligand, PH_3, by the stronger ligand, PF_3, did not then occur. All possible species from $Ni(PF_3)_4$ to $Ni(PH_3)_4$ may have been formed, but only $Ni(PF_3)_2(PH_3)_2$, $Ni(PF_3)_3PH_3$, and $Ni(PF_3)_4$ were stable enough to be pumped off the cold surface. There are many possibilities for the formation of complexes by condensation of a transition metal vapor with a mixture of two ligands; one a strong ligand capable of supplying a large part of the electronic requirements of the metal, the other a ligand too weak or thermally unstable to compete with the first in conventional preparative procedures.

An attempt to form the unknown compound $Cr(NO)_4$ by cocondensing a mixture of chromium vapor, NO, and BF_3, was not successful. The chromium was oxidized and formed no volatile product. The BF_3 was added merely to lower the vapor pressure of NO by forming a weak complex with it on the cold surface. More productive was the cocondensation of manganese vapor, NO, BF_3, and PF_3. The new compound $Mn(PF_3)(NO)_3$ was formed in a 25% yield (*36*). This compound could not be made using conventional high pressure techniques (*49*).

When nickel vapor was condensed with CO_2 at −196°, the resulting solid evolved CO rapidly on being warmed above −150°. About 10% of the nickel was recovered as $Ni(CO)_4$. The overall reaction was

$$Ni(g) + CO_2(g) \xrightarrow{\text{cocondense}} NiO + CO + Ni(CO)_4 \tag{36}$$

In this process, CO_2 can be considered to be the precursor of the ligand CO. Cocondensation reactions involving precursors of less common ligands, such as B_2F_4 as a source of BF (*69*) and Si_2Cl_6 as a source of $SiCl_2$ (*82*), are being studied currently in the author's laboratory.

A report by Burdett and Turner (*14a*) on the formation of nickel dinitrogen complexes, $Ni(N_2)_x$, from nickel atoms and nitrogen in a matrix at 20°K, illustrates further the range of compounds which can be made by low temperature reactions of metal atoms.

C. REACTIONS OF METAL VAPORS WITH ORGANIC LIGANDS

The condensation of chromium, iron, cobalt, and nickel vapors with cyclopentadiene at −196° has been studied (*91*). In each case a sandwich complex of the metal was formed as shown in Eq. (37). The yields based

$$\begin{gathered} Cr(g) + C_5H_6(g) \xrightarrow{\text{cocondense}} \underset{(50\%)}{Cr(C_5H_5)_2} + H_2 \\ \text{Fe: } Fe(C_5H_5)_2\ (70\%) + H_2 \\ \text{Co: } C_5H_6CoC_5H_5\ (50\%) + H_2 \\ \text{Ni: } C_5H_7NiC_5H_5\ (80\%), \text{ no } H_2 \text{ evolved} \end{gathered} \tag{37}$$

on the metal condensed are shown in parentheses. All these compounds can be made quite easily by conventional synthetic methods; so although the reactions with metal atoms are efficient, they are of little practical importance.

Chromium vapor reacted on condensation with benzene at −196° to form $Cr(C_6H_6)_2$ in about a 60% yield (*126*). No direct synthesis of this compound from chromium and benzene had been reported previously. Indirect preparations of $Cr(C_6H_6)_2$ have been known for many years [e.g., Fischer (*26*)]. A mixture of benzene and PF_3 condensed with chromium vapor at −196° gave good yields of $C_6H_6Cr(PF_3)_3$ (*36*).

The reaction between iron vapor and benzene at −196° was more complex than with chromium (*126*). A solid was formed which exploded on warming to about −40°. Iron and benzene were the main products of the explosion, but small amounts of diphenyl and hydrogen were also formed. The iron–benzene cocondensate was found to be chemically very reactive. On warming it from −196° in the presence of 1 atm hydrogen, there was no explosion and part of the benzene was reduced to cyclohexane. Condensation of cyclopentadiene onto the iron–benzene cocondensate at −196° resulted in the formation of ferrocene when the mixture was allowed to warm to room temperature. The results show that an iron–benzene complex was formed on the cold surface, but its formula and structure are not clear. There is no previous report of a zero-valent iron–benzene complex. Nickel vapor did not react at all with benzene at −196°.

It has been found that π-allylnickel halides can be formed very efficiently by condensing nickel vapor with allyl bromide or allyl chloride

$$\begin{aligned} \mathrm{Ni(g)} + \mathrm{C_3H_5Br(g)} &\xrightarrow{\text{cocondense}} \underset{(60\%)}{(\pi\text{-}\mathrm{C_3H_5NiBr})_2} \\ \mathrm{Ni(g)} + \mathrm{C_3H_5Cl(g)} &\xrightarrow{\text{cocondense}} \underset{(70\%)}{(\pi\text{-}\mathrm{C_3H_5NiCl})_2} \end{aligned} \qquad (38)$$

at −196° (*72*). These are useful preparations of these reactive complexes which compare favorably with conventional methods in speed and convenience.

Skell and Havel (*97a*) have reacted platinum vapor, formed in small amounts by vaporization of the metal from a tungsten filament at 1950°, with some unsaturated organic compounds at −196°. They report the formation of bis(1,5-cyclooctadiene)platinum(0) from 1,5-cyclooctadiene, $[PtCl(C_3H_5)]_4$ from allyl chloride, and ill-defined complexes with alkenes.

D. DEHALOGENATION REACTIONS OF TRANSITION METAL VAPORS

Copper is well known as a dehalogenating agent in organic chemistry. It is also used as a chlorine scavenger in the electrical discharge preparation of B_2Cl_4 (*61*). Thus, it seemed likely that copper vapor and possibly silver and gold vapors too, would be useful for dehalogenation in both inorganic and organic systems.

The first reaction to be studied was that between copper vapor and BCl_3 at −196° (*121*). Diboron tetrachloride was formed in yields varying from about 70% with a 20:1 mole ratio of BCl_3:Cu, to 40% with a 6:1 mole ratio. The work was initially carried with about 15 mmoles of copper, but it has been scaled up using the apparatus shown in Fig. 2. About 300 mmoles of copper, evaporated in 50 min, have been condensed with 2.7 moles of BCl_3 to form 57 mmoles of B_2Cl_4 (*128*). This is the best method available now for making B_2Cl_4, much more rapid than the discharge methods commonly used (*61*).

$$2Cu(g) + 2BCl_3(g) \xrightarrow{\text{cocondense}} 2CuCl + B_2Cl_4 \tag{39}$$

Silver vapor also reacts with BCl_3 on cocondensation at −196°, but the yield of B_2Cl_4 is very small. No B_2Cl_4 was formed from the reaction of nickel and BCl_3 at −196°, although an involatile solid containing combined nickel, boron, and chlorine was left after excess BCl_3 had been pumped off the cold surface.

The reaction of copper with substituted chloroboranes is also useful for making B–B-bonded compounds. Methyldichloroborane and copper vapor reacted at −196° to give high yields of 1,2-dichloro-1,2-dimethyldiboron, a liquid which is unstable above −10° (*121*).

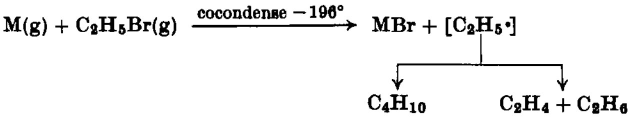
Copper vapor formed from molten copper heated in a crucible (Fig. 2) does not react with silicon–chlorine compounds at −196°. However, it has been found that if the copper vapor is formed by electron bombardment vaporization of copper, it will react with $SiCl_4$ to give perchlorosilanes. The reason for this difference in reactivity of copper vapor from the two sources is very likely the presence of excited copper atoms in the vapor formed by electron bombardment.

Both copper and silver vapors react very readily with PCl_3 at −196°. Some P_2Cl_4 can be pumped off from the cocondensates on warming, but

$$\begin{aligned} Cu(g) + PCl_3(g) &\xrightarrow{\text{cocondense}} CuCl(PCl)_x + \underset{(10\%)}{P_2Cl_4} \\ Ag(g) + PCl_3(g) &\xrightarrow{\text{cocondense}} AgCl(PCl)_x + \underset{(15\%)}{P_2Cl_4} \end{aligned} \tag{40}$$

most of the dechlorinated phosphorus species remain coordinated to the metal in highly colored solids (*108*). Attempts to form more P_2Cl_4 by displacement of coordinated PCl or PCl_2 groups with other phosphine ligands have not been successful.

The simple alkyl halides such as ethyl bromide are dehalogenated efficiently by copper, silver, or gold vapors at −196° (*28*). The general



$$\begin{tikzcd} M(g) + C_2H_5Br(g) \arrow[r, "\text{cocondense } -196^\circ"] & MBr + {[C_2H_5\cdot]} \arrow[d] \arrow[dr] & \\ & C_4H_{10} & C_2H_4 + C_2H_6 \end{tikzcd} \tag{41}$$

reaction with ethyl bromide is shown schematically in Eq. (41). Copper vapor formed mainly butane with traces of ethylene and ethane. Silver vapor gave mainly ethylene and ethane with a small amount of butane. Gold vapor gave butane and the ethylene–ethane mixture in equal amounts. These reactions are of no synthetic value, but copper does seem to be a fairly efficient reagent for causing coupling of carbon atoms rather than rearrangement of free radicals.

VI. The Method in Perspective

It was stressed in Section I that the emphasis of this chapter would be on low temperature reactions of high temperature species formed at low pressures under conditions which approximate to thermal equilibrium. This restricted scope was chosen because the synthetic uses of species formed this way have been mainly explored in the last few years. Before drawing conclusions about the value of these developments in chemical synthesis, it is important to consider some of the other synthetic techniques which involve the formation of "high temperature" chemical species as intermediates.

A. OTHER SYNTHETIC METHODS INVOLVING "HIGH TEMPERATURE" SPECIES

1. *Plasmas at Atmospheric Pressure*

Plasmas produced by an electric arc or induction heating may contain gaseous species in approximate thermal equilibrium at temperatures of 3000°–15,000°. These have attracted much attention over the last 20 years because of their potential for chemical synthesis on a large scale. Work in the area has been thoroughly reviewed (*39*, *50*, *76*).

Very few new compounds have been synthesized with the plasmas.

The main problem is quenching the hot gases fast enough to isolate metastable compounds. This is much more difficult at 1 atm pressure than under vacuum because of the large mass of gas to be cooled. The work of Stokes and Streng (*25*, *113*) on a liquid oxygen-quenched plasma is an exception.

2. *Low Pressure Electrical Discharges*

The apparent temperature of a gas in an electric discharge in the pressure range 10^{-2} to 50 Torr may be close to the ambient temperature. However, the gas will contain electrons and excited atoms and molecules with energies corresponding to temperatures of thousands of degrees (*76*). The excited or "high temperature" species present may not be of a type which could be formed under thermal equilibrium conditions. They will react with surrounding molecules in the gas phase or on cold surfaces. The rate of formation of the "high temperature" species is usually much lower than by thermal equilibrium methods.

Jolly (*38*) has reviewed the most important uses of discharges in synthetic inorganic chemistry. They have been particularly useful for forming catenated hydrides and halides, and, at low temperatures, for forming very unstable reactive compounds like oxygen and noble gas fluorides (*83*, *114*). In most cases both reactants and products are contained in, or pass through, the discharge. This is a severe limitation on the method as many compounds are polymerized or decomposed by the discharge. Some long-lived atomic species, especially nitrogen and hydrogen atoms (*38*, *85*), have been formed in discharges remote from the compounds with which they were reacted.

It was pointed out by Jolly (*38*) that discharge methods are not popular among synthetic chemists because of the complicated apparatus, the small yields of products, and the difficulty of predicting the course of reactions. These criticisms are true, in part, for all the synthetic methods involving high temperature species.

The process of sputtering metals and other materials by bombardment with excited argon atoms and ions, is another example of the formation of "high temperature" species by discharge processes (*141*). The species which cause transport of materials are mainly atoms or simple ions. This technique has not yet been used in the synthesis of compounds by low temperature cocondensation, although it could be very useful.

3. *Photolysis*

Photochemical excitation is widely used as a synthetic tool in organic chemistry, but not so much in inorganic chemistry. Excited or "high temperature" species are formed either by direct interaction of quanta with molecules or by transfer of energy from selectively excited atoms such as mercury (*15*). The selection of excitation energy is much easier than with electrical discharges and the processes which occur are generally better understood. However, as with discharges, the rate of production of excited species will be lower than in thermal equilibrium methods unless intense energy sources are used.

Photolysis can be carried out at any temperature or pressure, but usually both "reactants" and products are exposed to the radiation. It has been used to generate tiny amounts of new compounds for spectroscopic identification in matrices at temperatures of −196° or lower. Thus, carbon atoms formed from photolysis of cyanogen azide at 20°K, were reacted with hydrogen chloride to give HCCl (*37*).

$$\begin{aligned} N_3CN + h\nu &\longrightarrow C(^3P) + 2N_2 \\ C(^3P) + HCl &\longrightarrow HCCl \end{aligned} \qquad (42)$$

Atoms of Group VI elements can be formed conveniently photochemically. Gunning and his associates (*47*) have studied many reactions of sulfur atoms formed by photolysis of carbonyl sulfide.

4. *"Hot Atom" Chemistry*

"Hot atoms" are atoms with translational energies corresponding to temperatures of a few thousand to several hundred thousand degrees. The species of highest energy are commonly formed by nuclear transformations and recoil, e.g., $^{12}C\ (n,\ 2n)\ ^{11}C$. They cannot be made on a scale which is really attractive to synthetic chemists, but the mechanisms of their reactions have been extensively studied (*139*). Many of the products obtained by Wolfgang and his associates from reactions of "hot" carbon atoms with organic compounds are similar to those reported by Skell and his associates using carbon atoms formed under semiequilibrium conditions from an arc. This is to be expected as the "hot atoms" can lose their excess translational energy in collisions with other molecules.

B. CONCLUSIONS

The results of the synthetic work described in Sections III, IV, and V can be summarized by three points.

1. Reactions of high temperature species have formed a large number of new compounds many of which were only isolated successfully because of the low temperatures employed.

2. The work has been carried out on a scale which forms at least millimole quantities of products.

3. Some of the species used give high yields of products and their reactions are predictable. These can now be regarded as reagents and syntheses planned around them.

There is little doubt that the use of high temperature species formed under equilibrium conditions at low pressures is a fruitful exploratory method in chemical synthesis. As the high temperature species are formed apart from the compounds with which they are to be reacted, there are few restrictions on what reactions can be tried—in fact, far less restrictions than with the other methods using "high temperature" species discussed above.

However, the change from an exploratory to a widely applied synthetic method has not yet been made. The apparatus used so far has been too complicated and the techniques too sophisticated to have appeal to most chemists. There are some hopeful signs, particularly in reactions of transition metal atoms. Great simplification of the apparatus seems possible for these without sacrificing the scale of operation or the high yields of products.

The number of high temperature species which can be regarded as potential reagents is not unlimited. At the rate at which interesting areas of research can grow throughout the world, it should be possible to make a balanced judgment on the real importance of this area of work in about 5 years time.

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